

Appendix 1

Accelerated Removal and Validation Project (ARVP) Management

(Alan B. Copeland, Environmental Restoration Division, LLNL)

Project Development

This work was sponsored by EM-44 in the form of a \$1M supplement to the LLNL Environmental Restoration Division budget. This was made available in the September 1993 Financial Plan.

This funding came in response to an informal proposal dated August 3, 1993. The proposal contained three parts. Part 1 was to execute 3 months of continuous gasoline removal operations to take advantage of the elevated temperature of the site. Included in this part was further automation of the systems at TFF to reduce operating expenses, and temperature monitoring. The cost of this part was estimated to be \$900K. Part 2 was for additional characterization of the TFF site by boring 12 additional wells and analyzing the cores taken from them. This, with well completions, was estimated to cost \$900K. Part 3 was to do additional electrical or steam heating as indicated by the results of the additional characterization of the site in part 2. This was estimated to cost \$2.5M.

The proposed efforts were rescoped to fit the dollars made available, and the resulting plan, in the form of a critical path network, is shown in Figure A1-1. Part 1 of the proposal was included with a limited amount of automation planned. Part 2, site characterization, was not included. From part 3 of the proposal, we included preparation for using the four new wells that had been completed at the end of the second phase of Dynamic Stripping in a refurbished electrical heating network to heat the known cold spot in the center of the site.

In addition to the above, we planned to develop a computer model of the electrical heating and some geochemical properties measurements for use in the model. A brief air sparging campaign, designed to be very low in cost, was included to provide a basis for future work.

Project Team

The project team organization and principal participants are shown in Figure A1-2. Continuity with the work done during the Dynamic Stripping phases was provided by including key scientific, engineering, and technical personnel involved in those phases on the team.

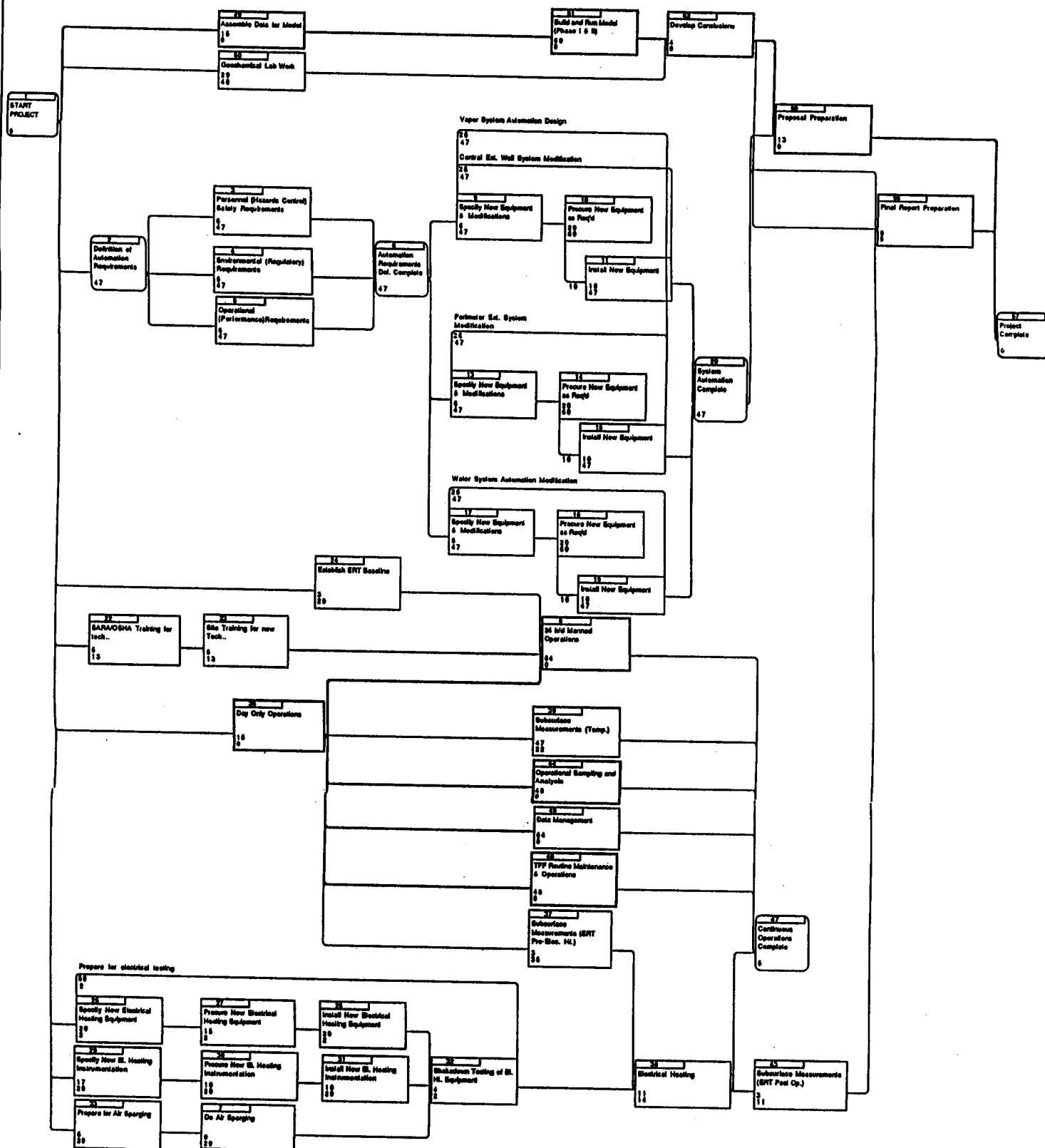


Figure A1-1. Critical path network for Accelerated Removal and Validation Project.

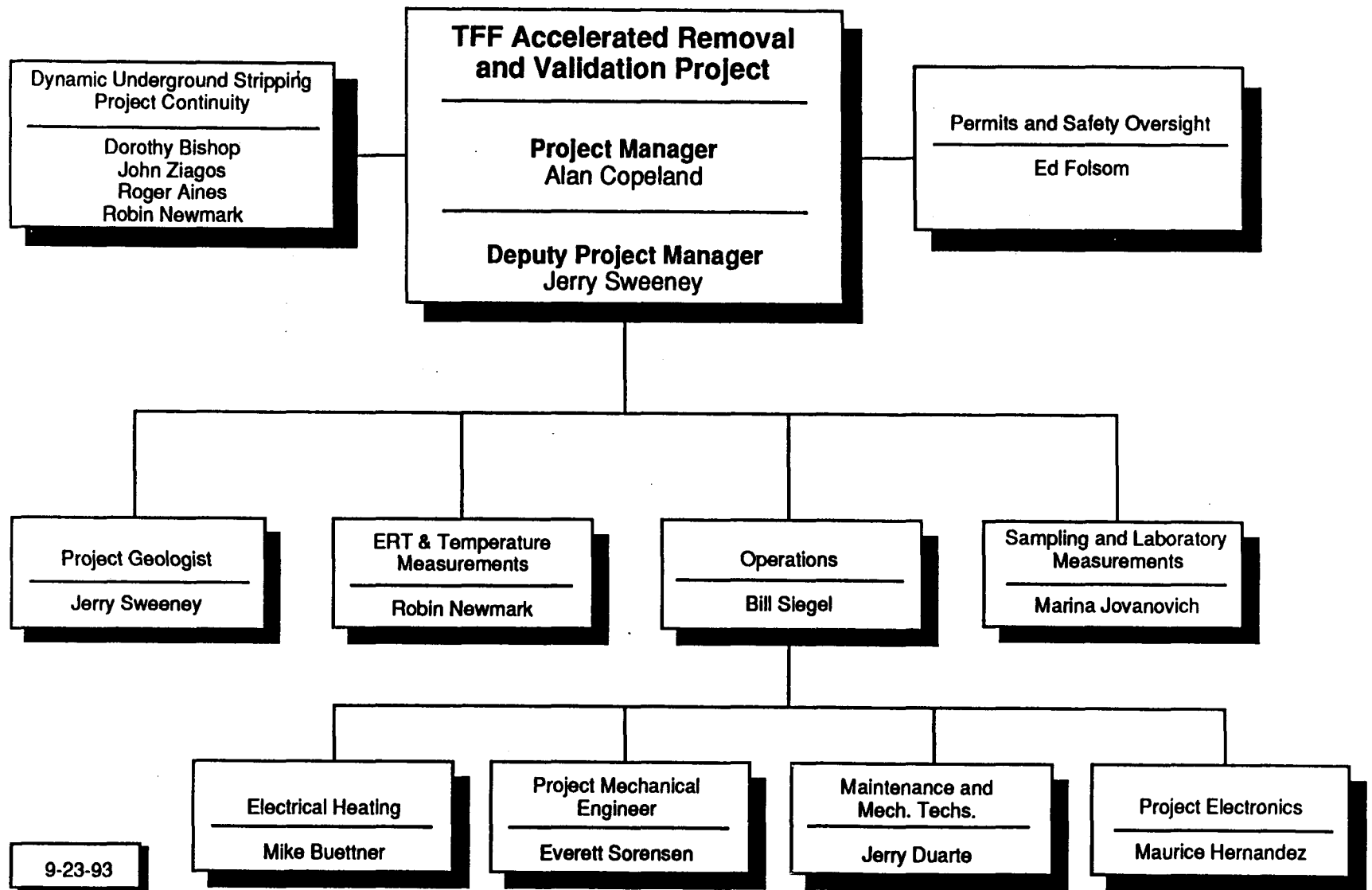


Figure A1-2. Organization chart showing project team and principal participants.

Project Execution

A timeline for project activities is shown in Table A1-1. As can be seen, both the air sparging and electrical heating operations were of very limited duration. This was due to the constraints of budget and the stipulation that these supplemental funds be expended prior to the end of the first quarter of FY94.

A plot of the project management parameters: Budgeted Cost of Work Scheduled (BCWS); Budgeted Cost of Work Performed (BCWP); and Actual Cost of Work Performed (ACWP) is given in Figure A1-3. The initial rate of accomplishment was higher than expected in the first 2 months. Overall, the project was completed on time and for the budget allocated. Some work done during the time of this project, which was related to the ongoing operations of TFF, was funded from the normal operating budget for the Livermore Site remediation. This averaged \$120K/month for September, October, and November.

A breakdown of the ARVP expenditure by project area is given in Figure A1-4. Preparations for electrical heating and 2 weeks of heating cost approximately \$100K more than was planned. The main reasons for this were unplanned scope of work in refurbishing the temperature logging systems, and the establishment of full displays and control of the pumping and treatment system operation in the control trailer for remote operation during electrical heating. As a result, the amount of general system automation completed to allow unmanned operation was less than originally expected. Also, offsetting the unplanned electrical heating expenditures were lower-than-expected operations costs from the use of adjusted workweeks instead of overtime for people covering the weekend operations.

Conclusions

The primary objectives as set out in the project plan were achieved. The time constraint of 4 months forced some project activities to be in parallel, which given more time would better have been done in series. For example, the computer modeling of both air sparging and electrical heating, had it been completed before the experimental work, might have altered the experiment plans for both. Also, more time to pursue the air sparging possibilities, while set up to do that, could have given more return for not much additional cost.

Table A1-1. ARV project timeline.

Date	Time	Activities
10/04/93	12:20 p.m.	Facility on line
10/18/93	10:30 a.m.	Vapor extraction stopped from GEWs-808 and 816
10/18/93	11:00 a.m.	Vapor extraction started from GIWs-813, 815, 818, and 820
10/26/93	—	GSW-16 isolated from vapor extraction system
11/02/93	3:45 p.m.	GIW-813 taken off-line
11/04/93	—	GIW-813 back on-line
11/05/93	—	Entire system shut down—power outage over weekend
11/08/93	11:00 a.m.	Facility restarted
11/09/93	—	Vapor extraction started from GSW-16, GEW-816, and GEW-808, vapor extraction stopped from GIWs-813, 815, 818, and 820
11/16/93	8:40 a.m.	Air sparging experiment started
11/16/93	11:00 a.m.	100% tracer recovery in GIW-815, 2% tracer at ICE
11/16/93	3:00 p.m.	End of first air sparging test
11/18/93	—	Extracting vapor from GIW-820 only
11/21/93	—	Electrical heating test run, voltages measured
11/22/93	11:00 a.m.	Air sparging restarted in GIW-815
11/22/93	3:30 p.m.	Stopped extracting from GIW-820
11/22/93	4:45 to 7:45 p.m.	Electrical heating system test
11/22/93	7:00 p.m.	Resumed extracting vapor from GEWs-808 and 816
11/24/93	—	Facility shut down for the holidays
11/29/93	8:00 a.m.	Ground water system restarted
	12:45 p.m.	IC engine restarted
11/30/93	7:00 p.m.	Electrical heating started
11/30/93	8:00 p.m.	Power outage, all systems down
12/01/93	6:30 a.m.	Electrical heating off
12/02/93	11:00 a.m.	Extracting vapor from the three central extraction wells (GSW-16 block removed)
12/03/93	6:10 p.m.	Electrical heating system operated overnight
12/07/93	5:00 p.m.	Electrical heating system operated overnight
12/08/93	4:55 p.m.	Electrical heating system operated overnight
12/09/93	5:00 p.m.	Electrical heating system operated overnight
12/10/93	5:00 p.m.	Electrical heating system operated overnight
12/12/93	9:00 p.m.	Extracting vapor from GIW-814, GIW-815, HW-1 & 2
12/13/93	—	ARV 24 h/day phase completed

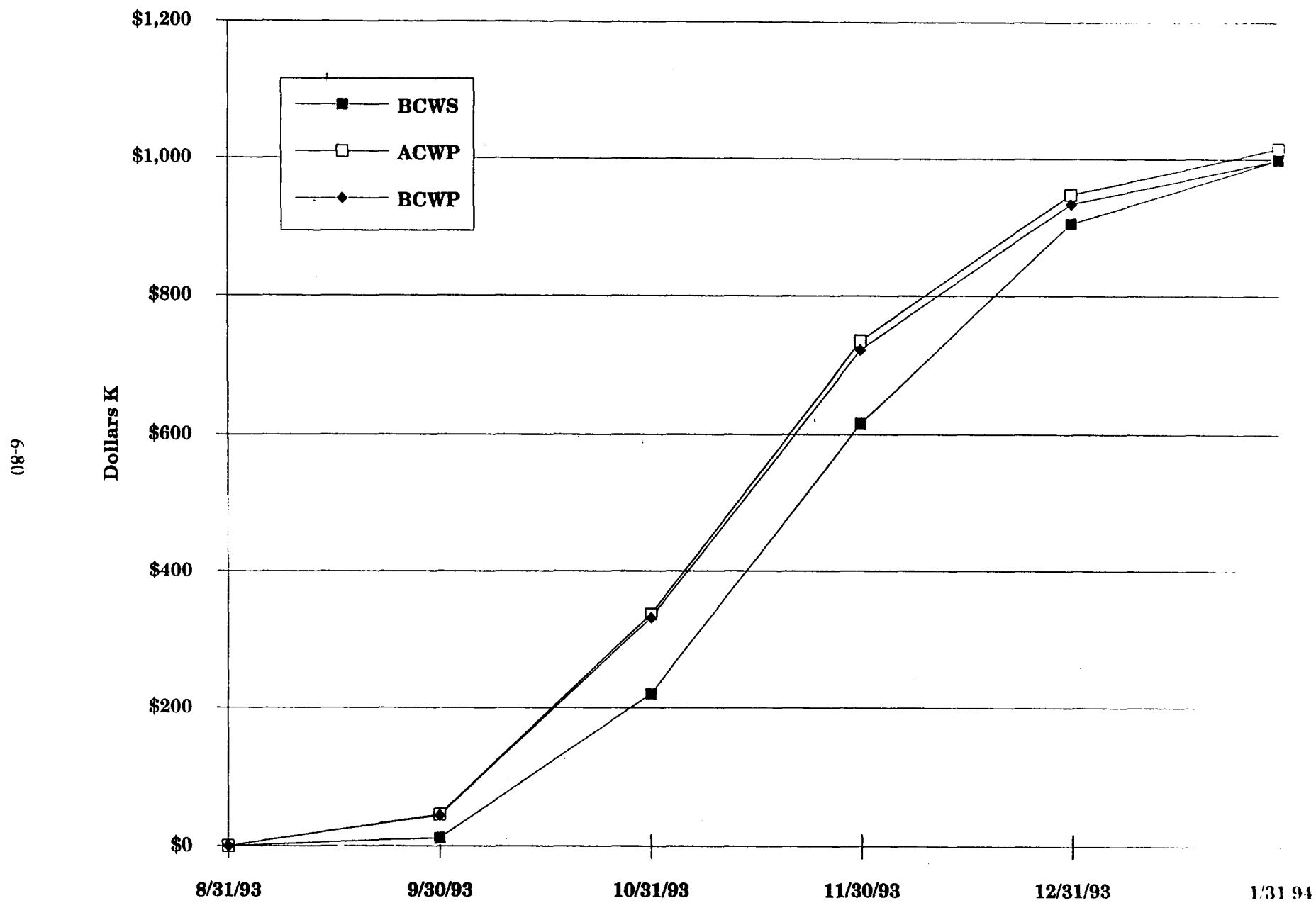


Figure A1-3. Earned Value for the Accelerated Removal and Validation Project.

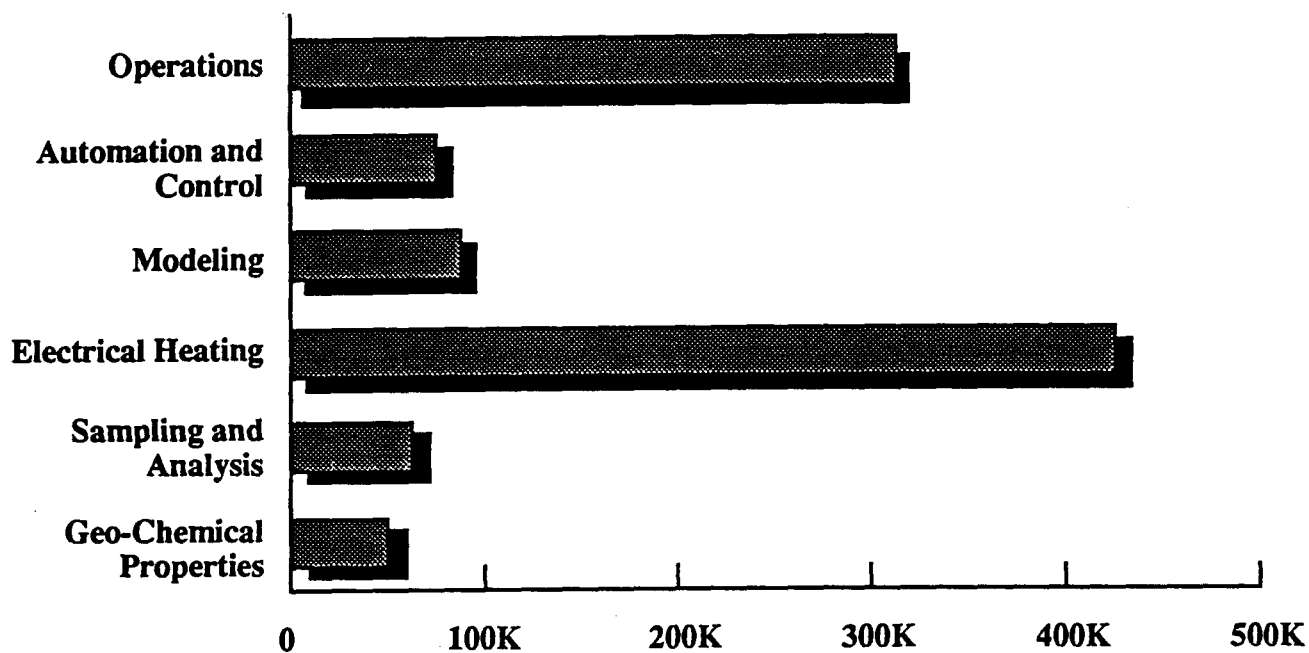


Figure A1-4. ARV project expenditures by major activity.

Appendix 2

System Automation

(Maurice Hernandez, Defense Science Engineering Division, LLNL)

This Appendix describes the present status of system automation efforts for TFF. This includes a brief historical design perspective and summary descriptions of the various automated control components. These are followed by recommended approaches to reaching the objective of safe, reliable automatic system operation.

Background and History

In 1988, TFF was constructed for an EPA-approved pilot study to evaluate vacuum-induced venting and treatment of FHC vapor. Vacuum-induced venting tests were conducted through 1991. The facility was subsequently modified for the DUSDP. When the Record of Decision was signed in August 1992, TFF was converted from pilot study to Remedial Action status.

Amidst these changes in the scope of TFF operations, we designed the main facility piping and instrumentation in early 1992, with construction taking place from June 1992 through January 1993. DUSDP modifications were designed and constructed between mid-1992 and October 1993. The activation phase of the main facility occurred between November 1992 and January 1993.

Due to the variances in operational scope and schedule acceleration brought on by the necessity for meeting regulatory milestones, a *critical path* approach was undertaken during the latter stages of the facility implementation phase. The idea behind this approach was to bring the system components on line as quickly as possible with manual control, while making provisions for a phased implementation of the automatic controls. Subsequently, budget and manpower constraints, as well as shifting priorities, have left TFF with the intended automatic capabilities only partially implemented. More information on the present status is given in the next sections.

Control System Status

Status is presented below for the various categories of the automatic control system.

Computers and Software

A 486-based personal computer (PC) with Genesis application software is presently in place at TFF. Genesis is a commercial software package designed for creating control system applications. The present software provides for a large percentage of the facility control, monitoring, and interlock needs. However, the implementation is best described as rudimentary, and some issues remain. These include long-term code maintenance, design documentation, code

verification and validation, flexibility for future modifications, and standardization with other ERD treatment facilities.

The operator software interface is identified as one further significant shortcoming. While nearly all pertinent information and control functions are available to the operator, it is not well presented. Graphic and functional limitations, ambiguous colors and symbols, and poor layout have made the interface nonintuitive and mistake prone. This also leads to significant training and retraining costs.

Instrumentation

The facility has been fully instrumented as specified by Remedial Design Report No. 2 (RD2). However, a more recently identified requirement (total effluent flow) has not been implemented, and several existing components must be repaired or modified. Examples include some that display erroneous or spurious readings (oil content monitor, LVB-60 influent flow, several thermocouples, demister effluent air flow), damaged sensors (GEW-816 well level transducer), and an improperly wired status/alarm panel. A comprehensive re-assessment of the control requirements may also identify additional instrumentation needs.

Safety and Interlocks

In general, the primary identified safety and failure mode considerations have been addressed, and there are no safety issues for *manual* operation. However, several interlocks that would be required for unmanned operation are routinely bypassed during manned operations due to uncertain performance and spurious false shutdowns. To date, a formal failure mode analysis for unmanned, standalone operation has not been carried out. cursory reviews have found that the present interlock system design is not inherently fail-safe, as dictated by the standalone design requirements. Other issues such as adequately meeting requirements for intrinsically safe installations, and facility electrical bonding and grounding have been reviewed for manned operation only.

Quality Control and Quality Assurance

Quality Control and Quality Assurance requirements for the facility are defined in the Remedial Action Implementation Plan (RAIP), RD2, and the ERD Quality Assurance Plan (QAP). Certain aspects of these are addressed in the present TFF design; however, these (system testing, document control, process monitoring) are carried out in a less formal manner than required for unmanned operation. Other requirements (QA/QC tracking, design control and changes, operating procedures, failure root cause analyses, and equipment calibrations) are not well established. Overall, a more formal approach is required for unmanned operation.

Recommendations

The following are recommendations to achieve a fully automated facility.

General

The overall facility control and monitoring requirements should be re-evaluated with respect to the present configuration and any foreseeable facility modifications. Some of the possible upgrades are identified in the RAIP and RD2. This must result in a formal agreement (i.e., a reviewed and approved document) enumerating the present needs, and providing for flexibility to implement future modifications. This document will also provide criteria against which ensuing designs and modifications are reviewed, and, as such, is subject to formal change control.

Computers and Software

Control software should be designed to meet the formal, approved requirements, using up-to-date analysis, modeling, and review techniques. This will provide assurances that design criteria are met, as well as establishing a design configuration baseline on which future additions and modifications can be based (design control). This will result in greater efficiency in maintenance and upgrades over the life of the facility.

The current Genesis application software should be replaced with the Paragon TNT package. This will standardize TFF with other LLNL treatment facility software, which will facilitate maintenance, and is necessary for networking.

Instrumentation

The problem areas described above must be resolved. The approved requirements will be used as a basis for the updated instrumentation design. It will likely also identify previously overlooked instrumentation needs, and perhaps eliminate some that are no longer applicable. The result will be a more comprehensive approach and a solid, robust design.

Safety and Interlocks

A comprehensive failure mode analysis must be done. The interlocks will then be designed to meet the identified needs and rigorously reviewed. Special emphasis will be placed on fail-safe implementation and provisions for operational issues, such as set points, alarms, and safe design of only *absolutely* necessary bypass mechanisms. Where possible, bypass mechanisms will be avoided. All identified special circumstances requiring bypass of normal interlocks will be implemented using specifically designed operational modes.

Installations will be thoroughly evaluated for intrinsic safety where required. Necessary modifications for strict adherence should be immediately undertaken.

Quality Control and Quality Assurance

Procedures must be put in place to meet the requirements of the RAIP, RD2, and ERD QAP. Care should be taken to meet the spirit and intent of the requirements, while not placing an unreasonable burden on facility personnel. Particular areas of concern are design documentation and control, design and modification reviews, and periodic inspections and maintenance.

Conclusions

Treatment Facility F requires a significant effort to reach true automated capabilities. A preliminary estimate totals \$330K (\$290K effort, \$40K equipment). While the costs incurred to make this effort are significant, the long-term gains should merit the expense.

Appendix 3

Electrical Heating Systems

(Ray McNairy, Defense Sciences Engineering Division, LLNL)

Instrumentation and Control

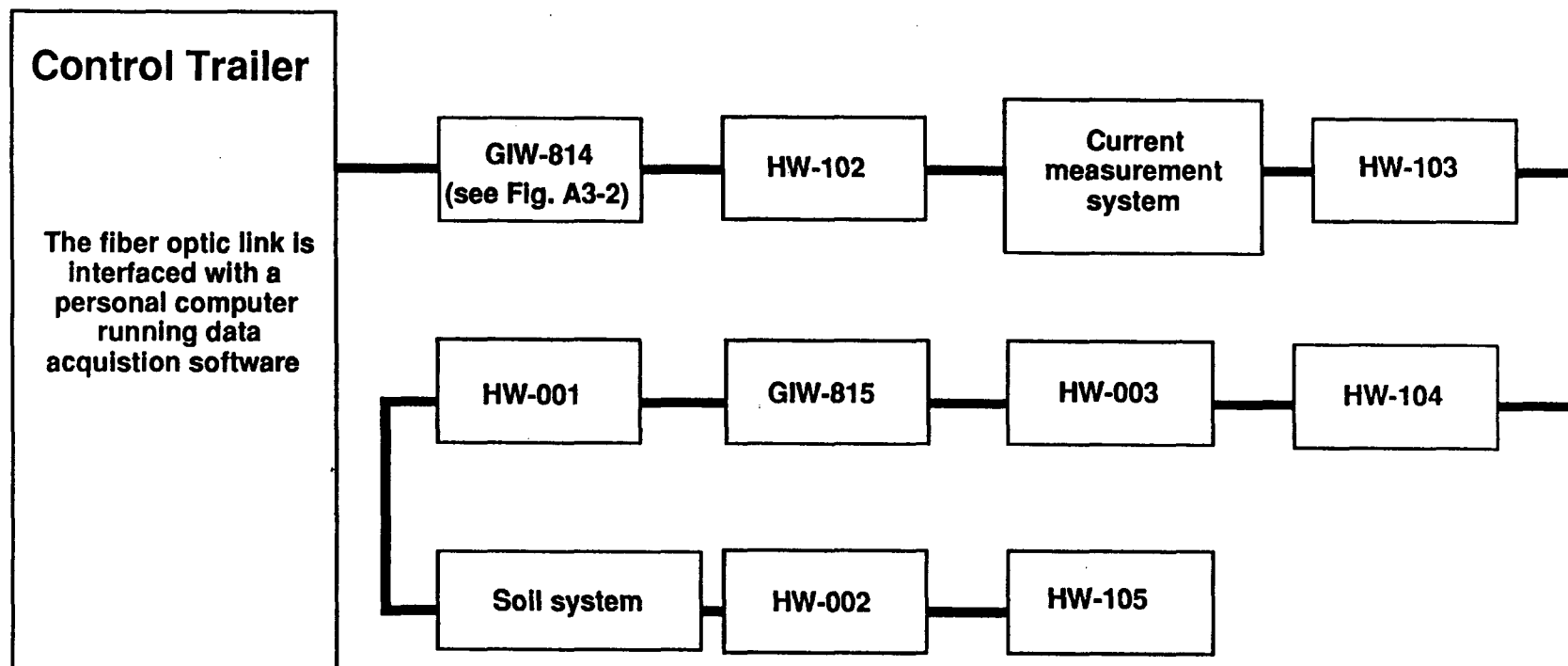
We developed instrumentation systems to monitor heater electrodes and soil temperatures for the ARV phase. The implemented system was designed to acquire real time data in a high-voltage, common mode environment where the electrode drive potential could appear at the low-voltage input of the instrumentation electronics. The electrode drive potential compromised the operation of the original data acquisition system. For this reason, we redesigned the entire system.

The heating system design required that 60 Hz power be applied to up to nine heating electrodes buried in the earth. The system had to handle electrode drive voltage levels of up to 600 VAC with current levels to 600 A. The system also had to record data from thermocouples grounded to the heating electrodes at discrete levels, thermocouples placed in nonheated "soil wells," as well as electrode drive current plus monitoring miscellaneous transducers as required.

Because of the maximum of 600-VAC electrode drive potential, the challenge was to reliably record millivolt-level thermocouple signals at a 600-VAC common mode potential. This common mode potential results from the thermocouple leads being grounded to the measured electrodes, thus exposing the thermocouples to the drive potential. In the new system design, we force the high common mode potential to appear across the instrumentation input power. This allows the electronics to be driven at the common mode potential of the individual electrode, thereby providing a low reference voltage for the system to operate against. The electronic system chosen was a commercially available OPTO-22 digital system controlled by Labview software. The OPTO-22 configuration was chosen for expediency because of the short development and fielding time allowed, and its successful use in past experiments. The OPTO-22 implementation was successful.

The OPTO-22 components are a modular instrumentation concept developed to serve the needs of the industrial process control community. As such, the system is extremely flexible and can condition and record large quantities of data at less than 10 channels/sec rates. Additionally, optical isolation is built in at the individual channel level; this allows a large latitude in transducer interconnection and configuration capability.

As configured (Figs. A3-1 and A3-2), each heating electrode has a dedicated OPTO-22 electronic front end for analog to digital conversion, scaling, and digital formatting of the millivolt level thermocouple data. Data communications to the individual electronics systems are accomplished with bidirectional digital fiber optic links to a control and archiving Mac II



See Figure A3-2 for typical internal sytem configuration at each location.

Figure A3-1. Configuration of the optical fiber system used to monitor temperatures and electrical currents at various wells at the TFF site.

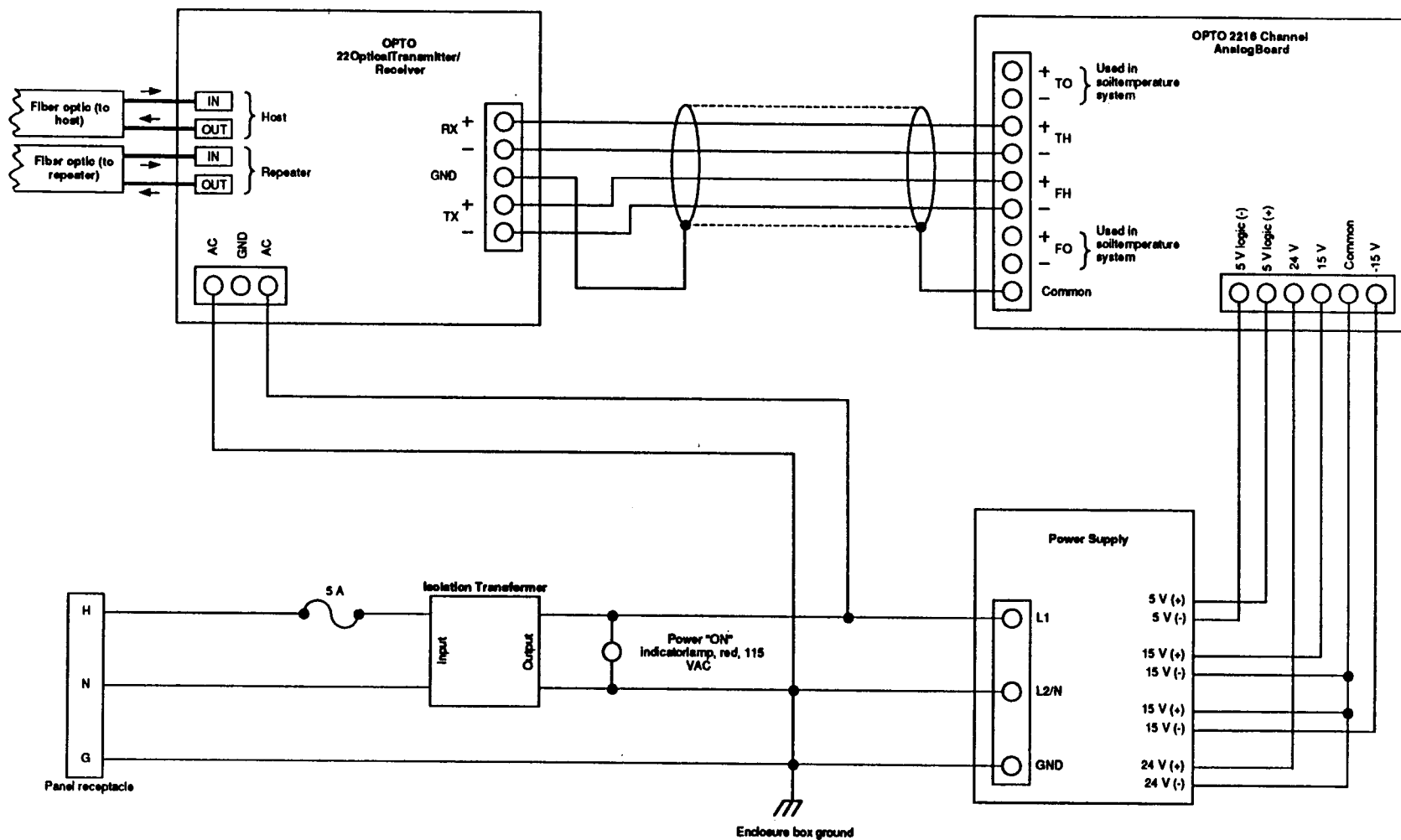


Figure A3-2. Detail of the internal power isolation system at each well location shown in Figure A3-1.

computer in the control trailer. The links are in a "daisy chain" configuration and conform to an industry standard data protocol, RS-488. The optical data link portion is a component of the OPTO systems concept.

Soil thermocouples are recorded by an additional, larger, OPTO-22 system of similar configuration to that above. Because the soil measurement electrodes are not exposed to the high common mode voltages of the heating electrodes, multiple measurement locations were successfully recorded with a common system. The soil thermocouple was controlled via the same fiber optic link as the heating electrode units and the unit for the electrode current measurements.

Grounding the OPTO-22 chassis and the fiber optic link to the electrode is analogous to placing the systems in a "bottle" that then can operate independently of electrode drive potential up to the design level of 600 VAC. The instrumentation system performed as designed after minor startup problems and proved quite reliable during the active heating phase of the experiment.

The heating electrode instrumentation configuration has a 16-channel capacity. Only four of these channels are populated with the analog input modules required to condition the two types of thermocouples installed. The electrode current system is identical to the heating electrode system except that 12 channels are used to acquire data from the 12 electrode current measurements. The soil system is an expansion of the base line heating well system and incorporated a 6 by 16 channel capability, of which 80 channels were populated. Low-voltage power supplies were installed at each measurement location. These identical supplies provide additional flexibility and power isolation, if needed. Primary isolation is provided by an isolation transformer and power connectors, rated for 600 VAC operation but operated at 115 VAC levels. The power configuration conforms to the National Electrical Code and was reviewed and approved for personnel safety both for *in situ* operations and during bench checkout. When the heating electrodes are not operating, the safety ground for the system is provided by the system chassis connection to the electrodes, which are earth referenced. In addition, a ground wire is installed in all power input cables, except the heating well systems, for a safety chassis ground. During heating, safety was controlled by rigid administrative control and site access control procedures. We used Operational Safety Procedures that were developed and carried over from the original heating experiment.

Power System

(H. Michael Buettner, Engineering Research Division, LLNL)

The electrical power system used for ARV was the same one used for the DUSDP (with some modifications) and is described below. When DUSDP concluded, some parts of the electrical power system were removed. In particular, the main circuit breaker, which had been leased, was returned to the vendor. Also, some of the wiring was cut to expedite removal.

Before ARV began, we had to obtain another main circuit breaker, splice some of the wiring, and reroute some of the existing power cables to the new heating wells.

The electrical heating system derives its power from the LLNL grid. A block diagram of the power distribution system is shown in Figure A3-3. Power is supplied from the grid at 13.8 kV and applied to the primary side of a 1,500 KVA transformer by means of a 15-kV, 600-A load interrupter switch. The working voltages on the secondary side of the transformer are 208, 350, 480, and 600 VAC, 60 Hz, three-phase. These voltages were chosen to offer some degree of control over the electrode currents. The lowest value was selected to account for the lowest interelectrode resistance we expected to encounter, while the highest value was chosen because it was the highest practical voltage we could use without resorting to special high-voltage equipment and safety requirements.

The secondary voltage is switched ON or OFF by the main circuit breaker (5,000 A, 600 VAC, 3 pole) and transmitted by a wireway to a low-voltage switchboard. The switchboard contains 12 adjustable trip breakers (one per heating electrode), and it is at this switchboard that the secondary voltage and appropriate phase are assigned to each electrode. The detailed specifications of the electrical system may be found in Newmark *et al.* (1994).

References

Newmark, R. (Ed.) (1994), *Dynamic Underground Stripping Project LLNL Gasoline Spill Demonstration*, Lawrence Livermore National Laboratory, Livermore, CA (UCRL-ID-116964).

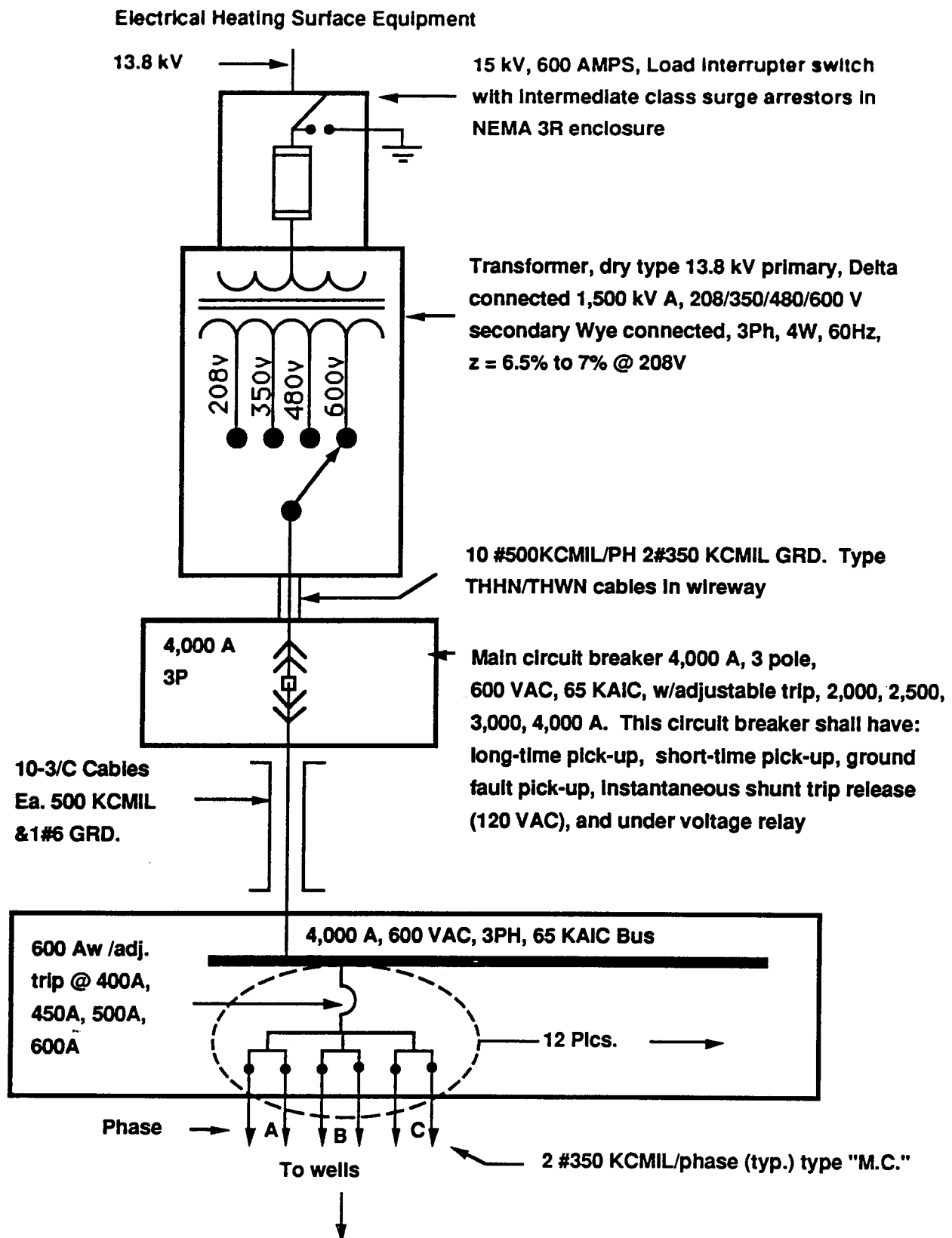


Figure A3-3. Diagram of the electric power system supplying power to the heater electrodes.

Appendix 4

Operational Measurements, Sampling, and Chemical Analyses

(Marina C. Jovanovich, Roger E. Martinelli, Health & Ecological Assessment Division, LLNL – Michael J. Dibley, and Kenneth L. Carroll, Environmental Restoration Division, LLNL – Everett Sorensen, Weiss Associates, Emeryville, CA)

This Appendix describes regulatory requirements, flow measurements, and chemical analyses for the ARV project at TFF. Data were collected primarily for measuring contaminant removal, experimental evaluation of the facility's performance under various operating conditions, and regulatory compliance verification.

Regulatory Compliance

Remediation of LLNL is enforced under CERCLA requirements by the Federal EPA, California EPA, the Bay Area Regional Water Quality Control Board (RWQCB), and others. Day-to-day operations of treatment facilities are regulated by the Bay Area Air Quality Management District (BAAQMD) and the Livermore Water Reclamation Plant (LWRP), which both required LLNL to obtain operating permits for the treatment facility.

To comply with discharge permits issued by the BAAQMD and the LWRP, we measured water and air discharge rates and analyzed these discharges for chemical composition. Table A4-1 summarizes regulatory compliance requirements for TFF.

BAAQMD. Three operations at TFF were permitted by the BAAQMD. These are the ground water treatment system air stripping discharge, the Continental Recovery Systems (CRS) regenerable carbon system, and the internal combustion engine (ICE). Each of these operations is restricted with individual operating conditions. These conditions include hydrocarbon concentration limits in the discharges; mass discharge limits for certain toxic compounds, such as benzene; destruction efficiencies; monitoring requirements; and record keeping.

LWRP. The LWRP is concerned only with the treatment facility's sewer discharge. The treatment facility was originally designed to achieve National Pollutant Discharge Elimination System (NPDES) discharge limits (natural receiving water discharge limits) established by the Federal EPA through the RWQCB. However, certain compounds in extracted ground water were not destroyed by UV/oxidation and were not completely stripped in the final air stripping stage. To operate the treatment facility and complete steam injection by the June 30 air district boiler exemption expiration date, LLNL researchers opted to discharge treated water to the sanitary sewer rather than attempt to improve the facility's performance to meet NPDES limits.

Table A4-1. Regulatory compliance requirements for LLNL Treatment Facility F.

BAAQMD

- Facility benzene discharge limit: 1.8 lb/day (confirmed monthly).
- E006-AQ counts towards total benzene discharge.
- Log book maintained daily (hours of operation, analytic results, carbon replacement).
- Source test required for CRS trailer within 30 days of startup.
- Permit posted in B406.

Sampling and Analysis Requirements:

Sample point	Method	Analyte	Frequency	Discharge limit
CFO	OVA/FID	TH	5/week	10 ppmv
E006-VPR (a)	OVA/FID	TH	5/week	10 ppmv
UVO5	EPA 601/602	TH/BTEX	1/month	Not Applicable (b)

Livermore Water Reclamation Plant (LWRP)

- 75 gpm maximum discharge rate, 50 gpm average.
- Permit posted in B406.

Sampling and Analysis Requirements:

Sample point	Method	Analyte	Frequency	Discharge limit
E006-AQ	EPA 624	BTEX	Quarterly	250 ppb
E006-AQ	EPA 625	Toxic organics	Annually	1,000 ppb
E006-AQ	EPA 6010	Metals	Annually	See list below (c)
E006-AQ	EPA 335.2	Cyanide	Annually	40 ppb

Notes:

- (a) CRS sampling only after startup.
- (b) Air stripper analysis for characterization, no concentration limit.
- (c) Metals discharge limits: As: 60 ppb; Cd: 140 ppb; Cu: 1,000 ppb; Total Cr: 620 ppb;
Pb: 200 ppb; Hg: 10 ppb; Ni: 610 ppb; Ag: 200 ppb; Zn: 3,000 ppb.

TH = total hydrocarbons.

BTEX = benzene, toluene, ethyl benzene, and total xylenes.

The LWRP requires quarterly analyses of the sewer discharge. The LWRP discharge concentration limits are considerably higher than NPDES limits and are therefore more easily achieved. Unfortunately, discharging to the sanitary sewer costs about \$7 per 1,000 gal discharged.

Since contaminant concentrations in extracted ground water have declined significantly since facility start-up, the facility now nearly achieves NPDES discharge limits in treated water. In December 1993, we analyzed the effluent for NPDES-regulated compounds. The only analyte detected above NPDES limits was manganese, detected at 780 ppb. The NPDES discharge limit for manganese is 500 ppb. Freon and acetone were detected at slightly elevated levels, but were attributed to chromatograph column cleaning solvents.

Current plans include continued NPDES compliance analyses to evaluate natural receiving water discharge options.

Contaminated Removal and Experimental Evaluation

For experimental purposes, we collected data to evaluate accurately the gasoline removal rate. This included frequent sampling and analyses of vapor and water at several points throughout the system and bi-hourly recording of operational parameters, such as flow rates, applied vacuum, temperatures, pressures, and gasoline accumulation. We analyzed each sample for its contaminant composition.

Ground Water and Vapor Sampling

During the ARV project, we sampled the aqueous stream twice per week due to low hydrocarbon concentration variability. Water analyses verified the aqueous gasoline removal rate and the UV/oxidation destruction efficiency. It also allowed estimation of the total gasoline discharge to the sanitary sewer, which amounted to less than 5 lb of gasoline in 11 million gal of treated water discharged in 1993.

Because the vapor system accounted for most of the gasoline removal and because it varied much more than the water stream, we sampled it daily, occasionally twice per day. Whenever a significant operational change was made, such as extracting from a different location, we analyzed the vapor stream before and soon after implementing the change. Vapor analyses allowed estimation of vapor-phase gasoline removal and verified air discharge permit compliance.

Sampling Equipment. Specialized sampling equipment was used for drawing samples under vacuum from the vapor system into plastic "tedlar" bags. Sampling bags were inserted into a desiccator equipped with plumbing from the sample bag to the sample port. By drawing air from the desiccator, a vacuum around the sample bag was created producing a pressure gradient from the pipes into the bag. Sample bags were equilibrated with atmospheric temperature and pressure after removing them from the desiccator. This automatic adjustment to ambient conditions allowed laboratory chemists to directly report chemical concentrations from GC data.

Sampling Error. We discovered several vapor sampling errors during the latter stages of the ARV project, resulting from a poor hose connection between the vapor sampling bag and the vapor piping. These errors occurred mostly when we extracted from any one “steam injection well” used originally for injecting steam around the gasoline spill perimeter. We extracted vapor from these wells to test hydrocarbon concentration variations vs extraction duration and for air sparging testing. Such extraction required greater applied vacuum. To collect a sample from the higher-vacuum piping, the leak potential increased. Ambient air occasionally leaked into sampling bags when poor sampling bag connections were made under these higher vacuum sampling instances.

After discovering this, we replaced the sampling apparatus with a more durable unit that passed pressure testing. Additional vapor samples collected for tracer analyses with a different apparatus simultaneously with the inadvertently diluted samples were later analyzed for hydrocarbons to validate the amount of dilution which occurred in early sampling scenarios.

Sampling Protocol and QA/QC. To prevent additional sampling errors subsequent to the initial effort, we produced a formal sampling protocol with written instructions on sampling apparatus operation. We performed regular vacuum testing of the sampling apparatus to ensure leak-tight sample collection. Occasionally, we analyzed duplicate and triplicate samples collected by different personnel only minutes apart to verify representative sampling methods. All of these quality assurance/quality control efforts indicated that we prevented additional sampling errors.

Chemical Analyses

Standard analytical methods were used for measuring total BTEX and total petroleum hydrocarbons (TPH). We diversified the analyses by using selective detectors and different gas chromatographs to aid in interpreting patterns of contaminant recovery from both the aqueous and vapor streams.

Sampling Ports. Figures 2 and 3 in the main text present simplified schematics of TFF showing sampling ports for the water treatment system and vapor treatment system, respectively. The following list describes each sampling port designation:

Aqueous Ports

TFF-SEPI	Oil/water separator (OWS) influent, located after the ambient air heat exchanger
TFF-UVI	UV/oxidation system influent
TFF-UV05	UV/oxidation system effluent
TFF-E006-AQ	Facility effluent to sanitary sewer, located after the air stripping tanks
TFF-MEGA-AQ	Aqueous phase obtained from vapor stream OWS (aqueous condensate from flat plate heat exchanger)

Gasoline Port

TFF-MEGA-HC Condensed gasoline obtained from vapor stream OWS ("organic" condensate from flat plate heat exchanger)

Vapor Ports

ICE-IN Internal combustion engine influent, located after the flat plate heat exchanger

ICE-OUT ICE effluent

TFF-CFI GAC filter influent (air stripping tank off-gas vapor effluent; aqueous stream)

TFF-CFO GAC filter effluent (vapor).

Table A4-2 summarizes the ARV project sampling schedule.

Table A4-3 summarizes the number of samples collected and the number of these samples analyzed for each sampling port during the ARV project.

Analytical Methods

This section describes analytical equipment used for chemical analyses during the ARV project.

Aqueous and Vapor Analyses

GC Apparatus. Chromatography was performed using a Hewlett Packard 5890 series II gas chromatograph (GC) outfitted with a photoionization detector (PID) and an electrolytic conductivity detector (ELCD). A low dead volume (LDV) injector port with a transfer line attachment from an O.I. Analytic Corporation Model 4560 Liquid Sample Concentrator (#6 trap, tenax/silica gel/charcoal) was interfaced to the GC. The GC column was a J & W Scientific 30 m x 0.53 mm (inner diameter), fused silica DB624, with a film thickness of 3 micrometers. The GC injector port temperature was maintained at 190°C. The PID and ELCD temperatures were maintained at 220° and 900°C, respectively. A PTA-30 W/S autosampler (Dynatech Precision Sampling Corp.) was employed for aqueous sample analysis. The GC oven temperature profile had an initial temperature and duration of 50°C for 5 min. The oven then ramped 6°C per minute to a final temperature of 110°C. A postsample analysis bake-out was employed by ramping the oven at 20°C/min to 170°C for 3 min. After the GC analysis, the oven returned to 50°C and equilibrated for 1 min prior to analyzing the next sample. The Liquid Sample Concentrator (purge and trap) was used for aqueous sample analysis and low VOC concentration vapor sample analysis. The purge, desorb, and bake times for liquid samples were 4, 3, and 20 min, respectively. The purge, desorb, and bake times for vapor samples were 8, 3, and 20 min, respectively. The purge, desorb, and bake temperatures for either liquid or vapor samples were 25°, 180°, and 190°C, respectively. HP Chemstation, an automated GC systems control and data acquisition programmable workstation, was used to gather, process, and archive the GC data.

Table A4-2. Sampling schedule.

System performance samples						
	Mon.	Tues.	Wed.	Thur.	Fri.	Analyses
Sample locations (aqueous)						
TFF-SEPI	1/d			1/d		TPH,601/602-EDB
TFF-UVI	1/d			1/d		TPH,601/602-EDB
TFF-UVO5	1/d			1/d		TPH,601/602-EDB
Sample locations (vapor)						
TFF-ICE-IN	2/d	2/d	2/d	2/d	2/d	FID**
	1/d§	1/d	1/d	1/d§	1/d	TPH

Regulatory samples

Sample locations (aqueous)						
TFF-UVO5	1/month					TPH***
TFF-E006-AQ	1/quarter					TPH,TTO, metal*
Sample locations (vapor)						
TFF-CFO	1/d	1/d	1/d	1/d	1/d	FID**

Notes:

* 1x/quarter-certified analysis (CLS).

** a field measurement.

*** 1x/month-certified analysis (CLS).

§ Include BTEX.

∞ Sampled during operation of carbon trailer .

Table A4-3. Sampling summary.

	Number of samples	Number of analyses
<i>Aqueous sampling port</i>		
MEGA	13	26
SEPI	19	38
UVI	19	38
UV05	19	38
E006	2	3
Total	72	143
<i>Vapor sampling port</i>		
ICE-IN	84	128
CFO	1	2
ICE-OUT	1	2
Total	86	132
<i>Wells</i>		
GIW-815	6	11
GIW-820	2	4
GIW-0820-Lower 7	7	8
GIW-820-Upper	12	16
Total	27	39

The compounds of interest in our aqueous analyses were BTEX, 1,2-dichloroethane, chloroform, carbon tetrachloride, trichloroethylene, and ethylene dibromide. BTEX and trichloroethylene were quantified by the PID. 1,2-dichloroethane, chloroform, carbon tetrachloride, and ethylene dibromide were quantified by the ELCD.

Aqueous samples were received for 601/602-EDB analysis from TFF-SEPI, TFF-UVI, TFF-UV05, and TFF-E006-AQ. The PTA-30 W/S autosampler was used to dilute (if necessary) and transfer the sample to the liquid sample concentrator. The dilutions performed by the autosampler were 1:5, 1:10, and 1:20. The final sample volume was 5 mL. Unpreserved aqueous samples were received in duplicate. One sample was analyzed immediately. The other sample was held for later analysis (confirmation purposes), or until its 2-week expiration date. Expired samples were returned to the sender for disposal.

Chlorobenzene was used as a surrogate to evaluate aqueous VOC recovery. Dichloropropylene was used as an internal standard to measure GC performance, and to generate the HP Chemstation internal standard sample concentration report.

Vapor samples were received in either 1-L tedlar bags or in 500-mL stainless steel spheres (SSS). Vapor samples were either introduced into the GC by direct injection into the LDV injector port (high VOC concentration samples), or through injection into the purge and trap (low VOC concentration samples). The sample was deemed as a low VOC concentration sample if the concentration was less than 50 ppmv. If the sample concentration was greater than 50 ppmv, it was deemed as a high VOC concentration sample. Duplicate injections were made on each sample. The injection volumes for low and high VOC concentration vapor samples were 20 mL and 10 microliters (μ L), respectively. Injections were made using either a 25- μ L or a 50-mL gas-tight syringe (Hamilton). The 25- μ L syringe was equipped with a side port needle, and the 50mL syringe was equipped with a Teflon stopcock (Supleco).

Low VOC concentration samples were introduced into the GC by injecting a 20-mL sample into the sparge tube (purge and trap) using a 50-mL Hamilton gas-tight syringe. The syringe was fitted with a stopcock and 18 gauge, 1.5-in, needle in order to remove the sample from the tedlar bag sample port. The syringe was flushed with the sample three times to ensure that a homogeneous vapor sample was entrapped within the syringe. Once a sample was drawn into the syringe, the stopcock at the syringe tip was placed in the off position. The needle was removed and the syringe was then attached to the purge and trap sparge tube. The syringe stopcock and the purge and trap sample port valve were then opened, and the sample was injected into the sparge tube. Once the sample was placed in the sparge tube, the purge and trap sample port valve was closed and the purge cycle started manually.

High VOC concentration samples were injected directly onto the GC with a 10- μ L sample through the LDV injector port using a 25- or 50- μ L Hamilton syringe equipped with a side port needle. The syringe needle was inserted into the tedlar bag sample port, and was flushed with sample at least three times to ensure that a homogeneous vapor sample was entrapped within the syringe. Ten microliters were drawn slowly into the syringe, and then the direct GC injection was made. The GC was started manually after sample injection.

Standards and Reagents

Neat compounds purchased from Chem Service, Inc., were used to prepare calibrations for aqueous and high VOC concentration vapor samples. Scotty's II certified vapor standards (1, 10, and 50 ppmv) were utilized to prepare calibrations for low VOC concentration vapor samples.

Aqueous. A 100-ppm (100 mg/L) working stock solution was prepared in 100 mL of high purity methanol (B & J Brand, Baxter Scientific Products). The working stock solution contained all compounds of interest. Working stock solutions were prepared in 120-mL clear glass serum bottles. The serum bottles were capped with Teflon-lined silicone septa and aluminum crimp caps. The septa and caps were replaced after use. GC calibration standards were prepared in 40-mL volatile organic analysis vials (VOAs) (I-Chem) by adding the appropriate volume of the neat reagent to 40 mL of ultrapure (0.22 micrometer filtered) water. The ultrapure water was acquired from a NANOpure ultrapure water system (Barnstead/Thermolyne), and purged with helium for 30 min before use. PID GC calibration standards from 2.5 to 2,000 ppb were prepared from a 100-ppm working stock solution. ELCD GC calibration standards from 2.5 to 100 ppb were prepared from a 100-ppm working stock solution. Calibration standards were analyzed and entered into the Chemstation for each dilution factor used. The GC was calibrated every 2 weeks, and GC calibrations were examined daily using calibration checks. Recalibration of the GC would occur any time the calibration check varied 10% from the anticipated value.

Vapor. When the sample was received, the VOC concentration range was determined by checking previous results or by GC screening. The sample designation and analytical method were then entered into the HP Chemstation. Standards were prepared in a 500-mL stainless steel sphere or 1-L tedlar bags. Neat compounds purchased from Chem Service, Inc., for uncertified standards were prepared to a desired concentration. Standards were made in the laboratory by adding the proper amount of clean air to the tedlar bag and injecting the appropriate quantity of neat VOC into the bag using a Hamilton syringe. The bag was then allowed to stabilize for 20 min prior to use. When the commercial standards were employed, a tedlar bag was filled with the vapor standard and analyzed by GC. Vapor standards were made daily and not reused beyond 24 h. Standards were analyzed weekly, and a response factor (RF) was used to calibrate the GC and quantify the vapor sample concentrations. The RF was checked during the week, and the GC was recalibrated if necessary.

TPH Analyses

Analyses of total petroleum hydrocarbons (TPH) were performed using an autosampler (PTA-30W/S, Dynatech Precision Sampling Corp.) and a purge and trap concentrator (Model 4460A, Trap #6: Tenax/Silica Gel/Charcoal, O.I. Corp.) coupled to a Hewlett Packard HP 5890 Series II GC equipped with a flame ionization detector (FID). A fused-silica column (30 m x 0.53 mm i.d.) coated with 1.5 μ m dimethylpolysiloxane (DB-1, CAT# 125-1032, J&W Scientific) was employed. The injector and detector temperatures were 200° and 220°C, respectively. The GC oven was held at an initial temperature of 35°C for 4 min followed by temperature programming to 80°C at 8 deg/min, then to 220°C at 12 deg/min, and then to 240°C at 20 deg/min with a final hold at 240°C for 2 min. The purge, desorb, and bake times were 11, 3,

and 20 min, respectively. The desorb and bake temperatures were 180°C. An HP 3365 Series II Chemstation (DOS) was used for data collection, storage, and integration.

Aqueous. Samples were injected into the purge and trap sparge tube via the autosampler in 5-mL aliquots. For samples of high concentration (i.e., TFF-MEGA-AQ, TFF-SEPI, and TFF-UVI), the autosampler was programmed to dilute the sample by a factor of 10 (4.5 mL water added to a 0.5-mL sample).

Vapor. Samples were injected directly into the GC in 100-μL aliquots via a 100-μL gas-tight syringe equipped with a side-port needle (Hamilton). For samples of low hydrocarbon concentration (i.e., TFF-ICE-OUT and TFF-CFO), the sample was injected into the purge and trap sparge tube via a 10-mL glass syringe. Two injections were made from each sample to ensure proper sample handling and representativeness.

Standards and Reagents. The sample of gasoline employed to calibrate the method was free product (weathered gasoline) obtained from well GSW-15 in June 1990 at LLNL.

Aqueous. A working stock solution (10,000 mg/L) was prepared in 100 mL of methanol (high purity, B & J Brand, Baxter Scientific Products) by adding 1.36 mL weathered gasoline (density = 0.735 g/mL). Standards were prepared from this working stock in the range of 250 to 25,000 ppm by adding 1 to 100 μL of this working stock to clean water (filtered by a NANOpure ultrapure water system, Model #D4741, Barnstead/Thermolyne; followed by a 30-min sparge with Helium) in 40-mL VOAs, (I-Chem). Appropriate standard concentrations and dilution factors (one to ten) were chosen that ranged between the concentrations of a given sample. Calibrations were run as required (generally monthly). Calibration checks were performed in triplicate prior to analysis of each set of samples, and the calibrations were deemed sufficient if each of the three check standards was $\pm 10\%$ of its expected value.

Vapor. Standards were prepared in 250-mL glass vessels. The glass vessels were equipped with two stopcocks and a septum port. A new septa was placed on the vessel, and the vessel was evacuated on the house vacuum for 30 min. The vessel was then removed from the house vacuum, and 1 to 10 μL of gasoline was injected into the vessel (resulting concentration: 832 to 8,320 ppmv). The vacuum was then relieved by a rapid turning of the stopcocks, and allowed to equilibrate for 30 min before analysis. Three standards of differing concentrations were prepared, and each one was injected twice (in 100-μL aliquots) to ensure proper sample handling.

TPH Window. For this experiment, TPH was defined as the concentration of all compounds that elute within the C₆ to C₁₂ window (hexane to dodecane).

Vapor. TPH was reported as mass per unit volume (mg/L or ng/μL) and parts per million by volume (ppmv). Reporting ppmv requires a molecular weight to convert mass/volume to ppmv (mol/mol). We report ppmv based on the molecular weight of hexane, 86 g/mol. The calculation is as follows:

$$\text{ppmv} = \frac{\text{Mass of gas/molecular wt. of gas}}{\text{Volume of air/molecular wt. of air}} \cdot 10^6$$

$$\text{ppmv} = \frac{\text{Volume } (\mu\text{L}) \times \text{density } (\text{g/mL}) \times 1 \text{ mL}/1000 \mu\text{L} \times 24.4 \text{ L/mol}}{0.25 \text{ L} \times \text{MW } (\text{g/mol})} \cdot 10^6$$

$$\text{ppmv} = \frac{4 \times 24.4 \times \text{density } (\text{g/mL}) \times \text{volume } (\mu\text{L})}{1000 \times \text{MW } (\text{g/mol})} \cdot 10^6$$

In the early part of the second phase of the DUSDP conducted at TFF (May through July 1993), some samples were observed to contain a large portion of low molecular weight compounds that elute prior to hexane and, therefore, outside of the TPH window. For these samples, we decided that the TPH value gave an inaccurate picture of the total amount of organic compounds in a given sample. For this reason, we defined a new value, which we termed "total hydrocarbons." The window for total hydrocarbons can be described as C₁ to C₁₂ (methane to dodecane), because we included all compounds that elute prior to dodecane in this calculation.

Field measurements were made using a Foxboro organic vapor analyzer (OVA) equipped with an FID. These measurements provided approximate hydrocarbon concentrations in discharged air for regulatory compliance.

Quality Assurance/Quality Control (QA/QC)

Water Analysis QA/QC

Surrogate Recoveries

Chlorobenzene was used as the surrogate spiking compound, and was added to every aqueous sample, including blanks. Project methods called for QC limits ranging between 80 and 120% of recovered surrogate, in compliance with EPA recommendations. Table A4-7 shows recoveries were always between the QC limits (EPA, 1988).

Field Spikes (Percent Recovery)

For analytical QA/QC, matrix spikes and matrix spike duplicates were performed throughout the duration of the experiment. The spiking levels were twice the estimated amount for designated compounds present in the sample. The spiking compounds were added to the matrix spike and matrix spike duplicate aliquots of the sample before being placed on the purge-and-trap apparatus.

Internal Standard

The Internal Standard Method (ISTD) using the HP3365 Series II Chemstation Software calculates each peak separately and reports the absolute amount of material for each calibrated analyte. The results are independent of sample size, giving the most accurate analysis scheme for liquid samples. The internal standard, cis-1,3-dichloropropene, was added in a known

amount to every sample. Because this internal standard was present in both unknown and calibrated samples, its presence was detected in all analyses and served as a reference or normalizing factor.

Internal Standard Calculation

Actual amount of y = Amount ratio x Actual amount of ISTD x M where:

$$\text{Amount ratio} = \frac{(\text{Area})_y}{(\text{Area})_{\text{ISTD}}} \times \frac{(\text{Response})_y}{(\text{Response})_{\text{ISTD}}}$$

- M is the multiplier specified on the calibration setting panel.
- (Area) y is the area of peak y.
- (Area) ISTD is the area of the internal standard peak.
- (Response) y is the amount per unit area of peak y.
- (Response) ISTD is the amount per unit area of the internal standard peak.

Detection Limits

Limits of detection (LOD) were set using the American Chemical Society recommendation that detection levels be set at three times the standard deviation of the noise level of the analytic measurement and that quantification levels be set at ten times the standard deviation. The range between three and ten times the standard deviation is considered uncertain for the purposes of quantification. GC limits of detection are primarily governed by the detector employed, detector sensitivity to the compound of interest, and sample volume. The LODs can be found in Table A4-4, which presents detection limits for various VOCs by detector type (*Analytic Chemistry*, 1983).

Table A4-4. Detection limits.

VOC	Photoionization detector (PID) (µg/L)	Electrolytic conductivity detector (ELCD) (µg/L)	Flame ionization detector (FID) (µg/L)
Benzene	0.2		
Toluene	0.2		
Ethyl benzene	0.2		
p,m-xylene	0.2		
o-xylene	0.2		
1,2-dichloroethane		0.2	
Trichloroethene	0.2	0.2	
Ethylene dibromide		0.2	
Chlorobenzene	0.2	0.2	
TPH			10

Criteria for Recalibration

Calibration checks were run daily using 25, 100, 2,500 µg/L of a list stock solution, which contained BTEX, 1,2-dichloroethane, trichloroethene, and ethylene dibromide. If the calibration check standards varied by 10% of the anticipated value, the instrument was recalibrated. All methods were calibrated by external calibration procedures using five to seven analyte concentrations. A National Institute of Standards and Technology (NIST) traceable external check sample was analyzed when a new calibration was performed.

Accuracy and Precision

Data quality criteria established in terms of precision and accuracy are presented in Table A4-5. Precision objectives are expressed in terms of relative percent difference (RPD). RPD is defined as the difference between two values, divided by their average. Precision was determined through the use of laboratory duplicates. The analyses of the duplicates met the analytical precision objectives of the project, which were $\pm 20\%$.

Accuracy objectives were evaluated through the use of laboratory control samples and matrix spike/matrix spike duplicate analyses. Laboratory control samples are clean reference samples spiked with a known concentration of target analytes.

Table A4-5. Data quality criteria and objectives.

Parameter	Precision (RPD)	Accuracy (matrix % recovery)
TPH	3	80 - 120
Benzene	2	80 - 120
Toluene	2	80 - 120
Ethyl benzene	2	80 - 120
?, m-Xylene	2	80 - 120
o-Xylene	2	80 - 120

Blank Analyses

Method blanks were analyzed for every three to four unknown samples showing no contaminants greater than the detection limit for the method being used.

Vapor Analysis QA/QC

Blank Spheres

Prior to use, 500-mL stainless steel spheres (SSSs) were cleaned, pressure checked, and analyzed for contaminants. Contaminated SSSs were flushed with clean air for 45 min to remove residual contamination. After the flushing, the valves were closed. GC analysis was then

performed using an equal or larger sample than required by the method being performed. FID and PID/ELCD detectors were used to check for residual contamination.

Precision

The data quality criteria are established in terms of precision (see Table A4-6). Vapor samples were not spiked; therefore, accuracy was not calculated.

Precision objectives are presented in Table A4-6. From duplicate analyses, the average difference, or average range, is calculated by summing all the differences (absolute values) and dividing by the number of observations: $R = \sum d_i/n$. This is converted to standard deviation(s) by dividing by 1.128.

Table A4-6. Data Quality Criteria and Objectives

Parameter	Precision (s)
TPH	2.3
BTEX	2.7

Criteria for Recalibration

All analytical methods used were calibrated by external calibration procedures, using two to three standard concentrations, depending upon the method. A new calibration was performed at least once per quarter or as needed when the response factors varied by 10% of the anticipated value. Calibration checks were run daily using 10 and 50 mg/L BTEX external standard purchased from Scotty Specialty Gas, Inc.

Ground Water Analytical Results

This section describes BTEX and TPH trends for various ground water treatment system sampling reports.

SEPI is the designation for the untreated ground water sampling port located after the ambient air heat exchanger (Fig. 2, main text). Early in the ARV project, TPH concentrations in extracted ground water were around 7 ppm. TPH concentrations increased to 20 ppm by the third day of continuous operation and then decreased to between 5 and 10 ppm for the remainder of continuous operations (Fig. A4-1).

Total BTEX concentrations in extracted ground water showed a similar trend to TPH concentrations, starting around 3 ppm and increasing to about 8 ppm by the third day (Fig. A4-1). Concentrations averaged about 3 ppm for the remaining 67 days of continuous ground water pumping. Total BTEX constituted about 35% of TPH except for an increase to about 75% on day 38. A 2.8-fold increase in total BTEX concentration was observed between days 36 and

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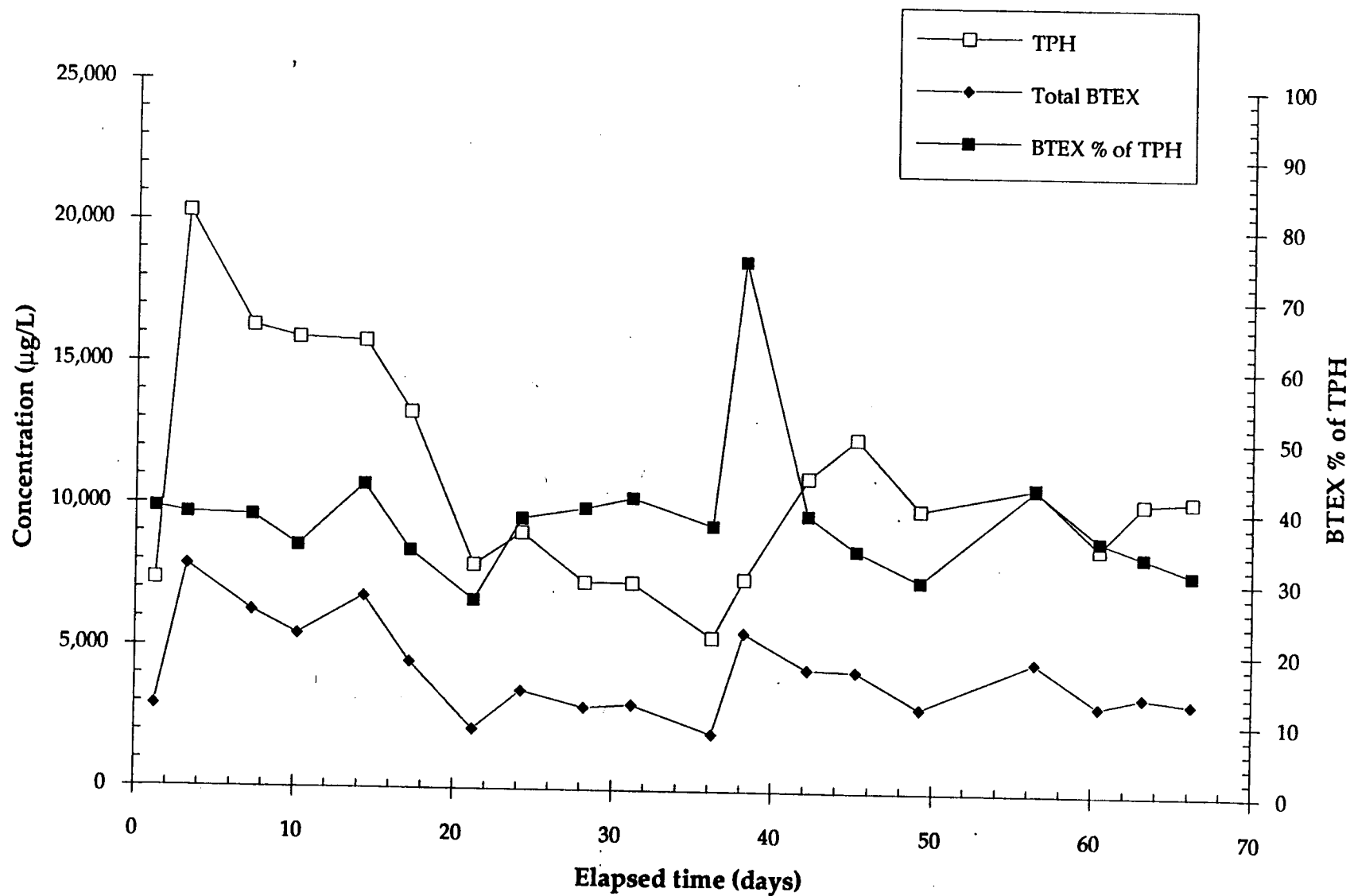


Figure A4-1. Aqueous TPH and total BTEX concentrations measured from the SEPI sampling port during ARV.

38, while only a 1.4-fold increase in TPH was observed. The data point may be an outlier except that the original chromatogram for BETX analysis shows a large increase in benzene.

The highest percent of the BTEX components in the aqueous stream consisted of toluene averaging about 36% with maximum concentrations of 2.9 ppm (Fig. A4-2). Total xylenes were also high and averaged 46% of total BTEX with a high of about 3.2 ppm. Benzene averaged 12% of total BTEX, ranging between 0.2 and 1 ppm during the 70-d period. Ethyl benzene constituted 7% of total BTEX with concentrations between 0.1 and 0.6 ppm during the same period.

The TCE concentration in extracted ground water averaged about 21 ppb. We detected no 1,2-DCA or EDB during the ARV continuous operations (Fig. A4-3).

UVI is the designation of the aqueous sampling port before entering the UV/H₂O₂ oxidation system and downstream of SEPI (Fig. 2, main text). Concentrations of TPH and total BTEX at UVI followed the same pattern as those at the SEPI port, but were usually lower by 20% or less (Fig. A4-4). Percentages of the BTEX components were similar to percentages measured at SEPI except ethyl benzene was as low as 3% and xylenes as high as about 54% of the total.

TCE concentrations in UVI were typically 24% lower than from SEPI. EDB and 1,2-DCA were not detected in UVI samples above 4.0 ppb.

UV05 is the designation of the aqueous sampling port located downstream of the UV/H₂O₂ oxidation system (Fig. 1, main text). UV/oxidation destruction efficiencies were calculated using BTEX concentrations measured from the UVI and UV05 sampling ports. BTEX destruction efficiencies greater than 90% were achieved during the first 24 days of continuous pumping (Fig. A4-5). Destruction efficiencies then decreased from 94% to about 26% during the following 46 days. Total BTEX concentrations in the UV/oxidation effluent varied between 0.03 and 3 ppm.

UV/oxidation destroyed 50% of the extracted TCE (Table A4-7).

Treated ground water was monitored at the E006-AQ port (Fig. 2, main text) before being discharged to the sanitary sewer after air stripping. BTEX, 1,2-DCA, and TCE were not detected in the samples collected from this sampling port.

MEGA-AQ is the designation for the condensed and separated water sampling port located downstream of the small oil-water separator (Fig. 3, main text). We began sampling the aqueous effluent 14 days after continuous operations began. The TPH concentration in separated water was about 65 ppm, decreasing to about 43 ppm after 21 days, and remaining fairly constant at 42 ppm for the remaining 49 days (Fig. A4-6). Total BTEX concentrations remained constant around 10 ppm throughout the 70-day project (Fig. A4-7). The composition of BTEX compounds in separated gasoline was typically about 5% benzene, 8% ethyl benzene, 28% toluene, and 59% total xylenes.

Vapor Treatment System Analytical Results

Sample concentrations changed over time as the facility was extracting VOCs. Generally, samples collected from ICE-OUT and CFO contained low VOC concentrations, and samples

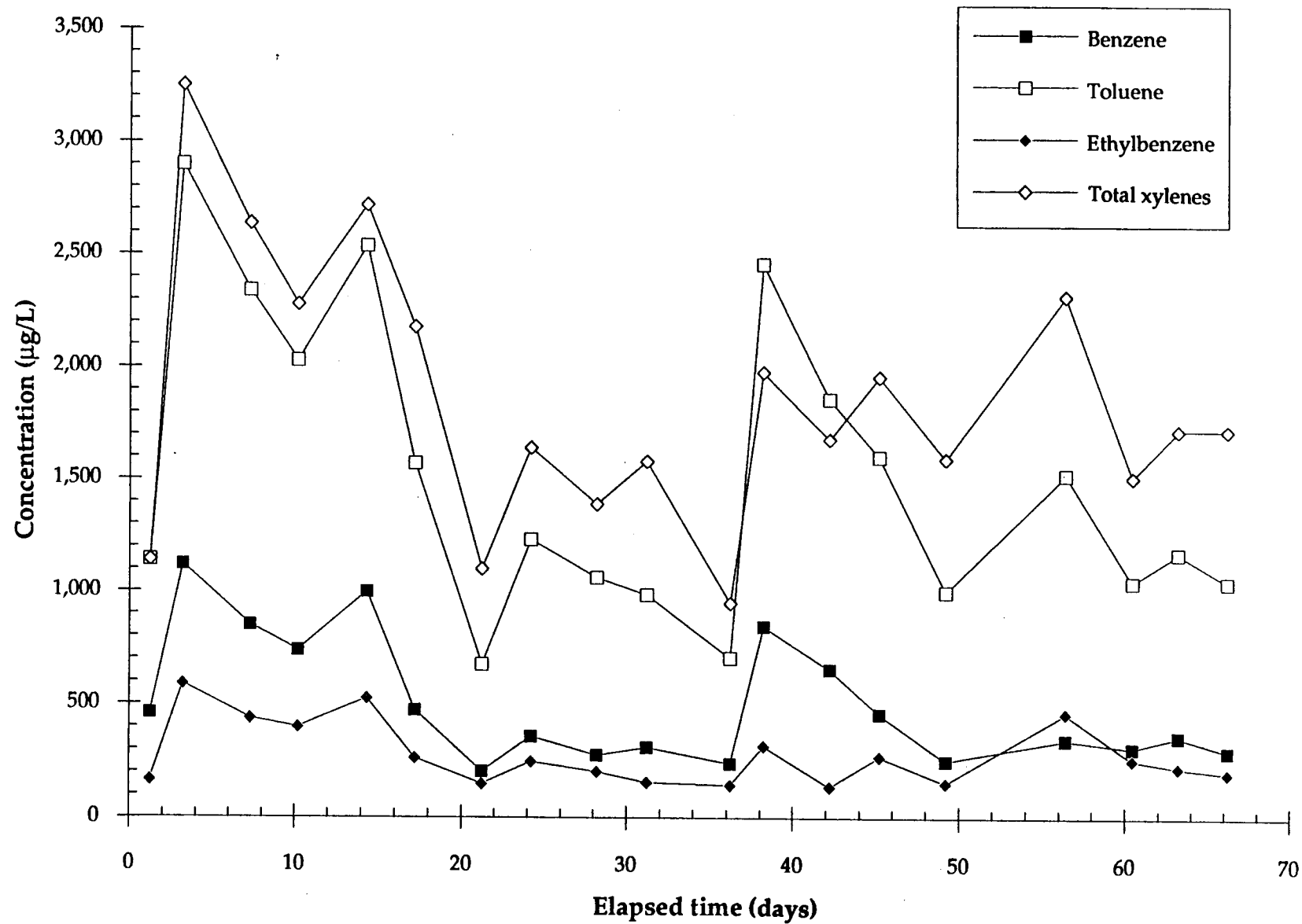


Figure A4-2. BTEX component aqueous concentrations measured from the SEPI sampling port during ARV.

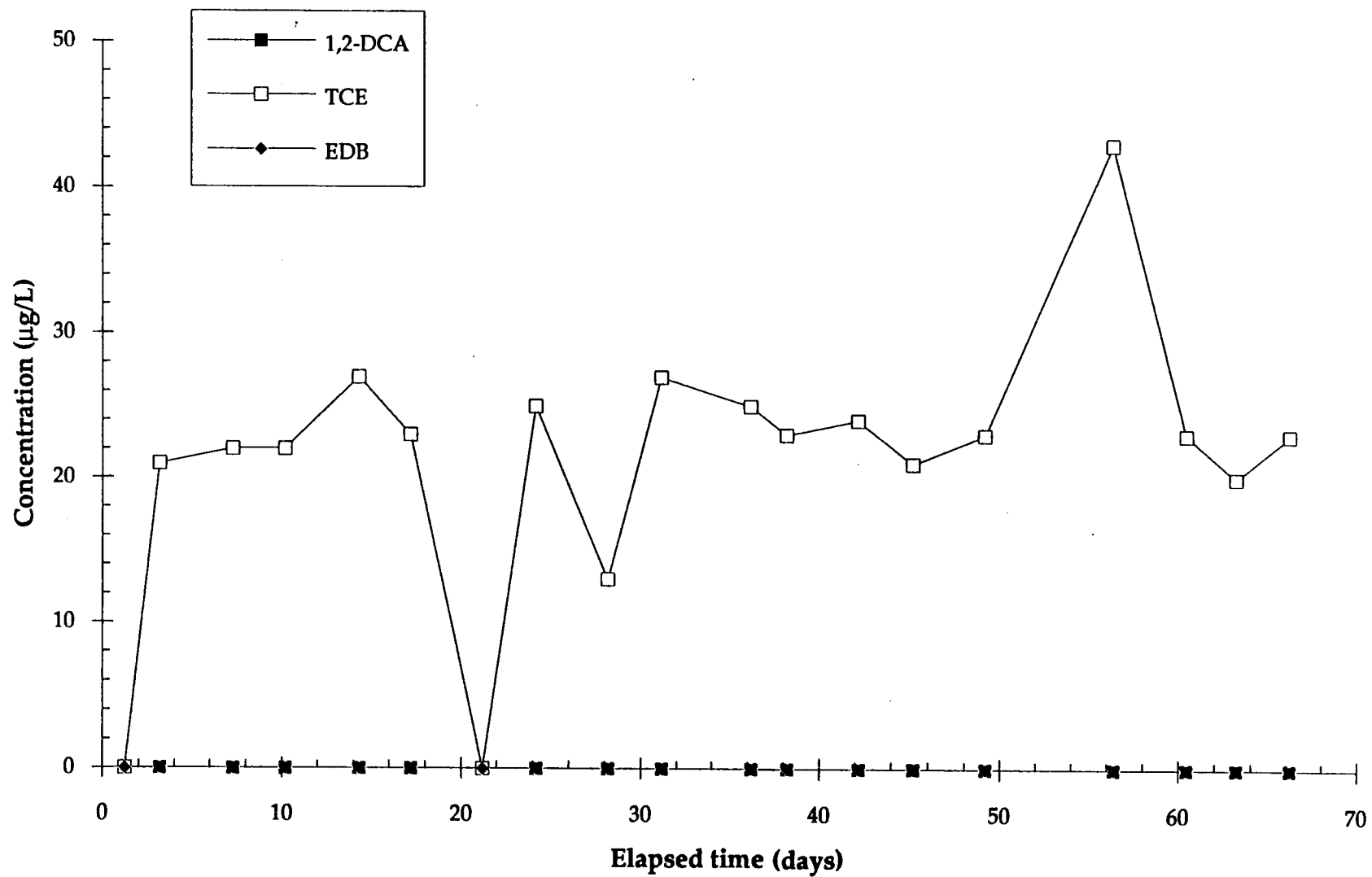


Figure A4-3. 1,2-DCA, TCE and EDB aqueous concentrations measured from the SEPI sampling port during ARV.

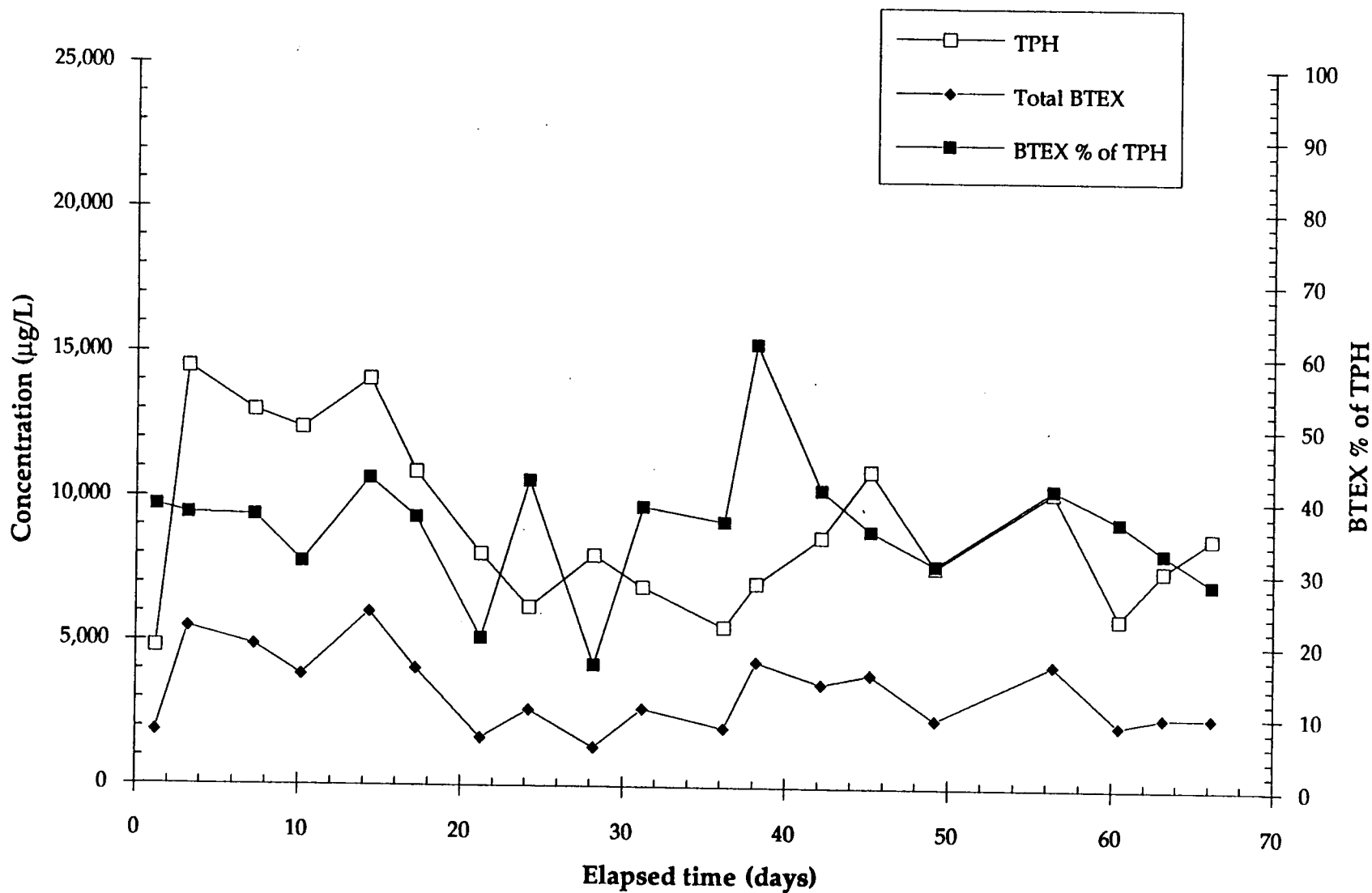


Figure A4-4. Aqueous TPH and total BTEX concentrations measured from the UVI sampling port during ARV.

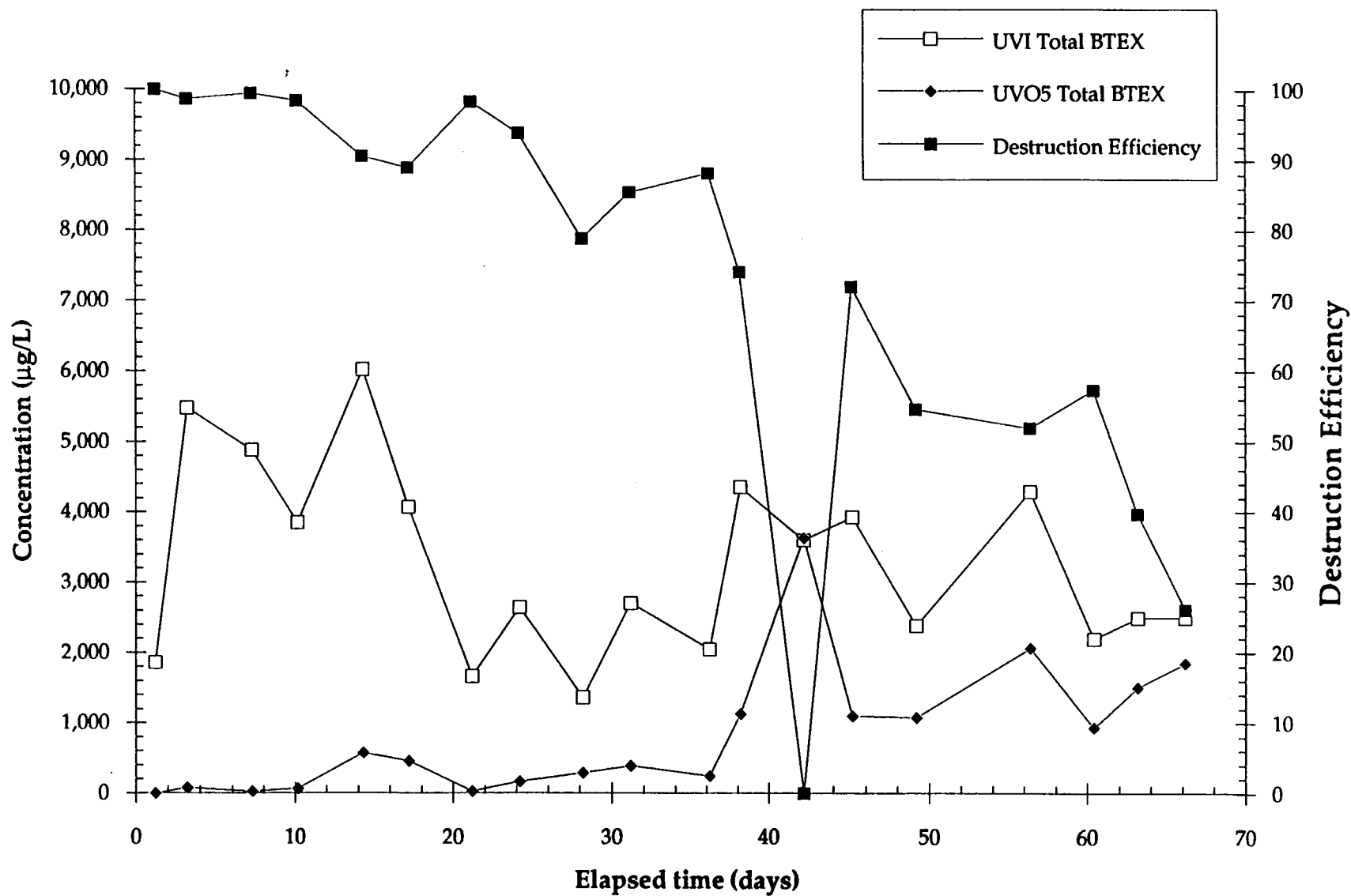


Figure A4-5. Aqueous-phase BTEX concentrations measured from TFF-UV1/TFF-UV05.

Table A4-7. ARV project aqueous analytic results.

Date sampled	Elapsed time (days)	Total BTEX (µg/L)	BTEX (% of TPH)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	Total xylenes (µg/L)	TPH* (µg/L)	1,2-DCA (µg/L)	TCE (µg/L)	EDB (µg/L)	Surrogate** (% recovery)
TFF-MEGA-AQ												
10/18/93	14.38	12,500	19.3	586.0	3,530	993.0	7,420	64,800	ND	ND	ND	80
10/21/93	17.21	12,600	25.1	609.0	3,480	1030.0	7,490	50,100	ND	ND	ND	94
10/25/93	21.21	10,600	23.2	485.6	2,910	856.2	6,320	45,700	ND	ND	ND	91
10/28/93	24.21	12,000	28.0	578.0	3,400	1020.0	6,970	42,800	ND	ND	ND	110
11/01/93	28.21	11,400	26.9	494.0	3,140	938.0	6,780	42,400	ND	ND	ND	95
11/04/93	31.21	11,900	26.7	590.0	3,400	990.0	6,870	44,500	ND	ND	ND	110
11/09/93	36.21	9,800	22.6	480.0	2,750	835.0	5,740	43,400	ND	ND	ND	91
11/11/93	38.21	8,420	20.5	404.0	2,340	659.0	5,020	41,000	ND	ND	ND	87
11/15/93	42.21	8,640	18.9	347.0	2,530	680.0	4,880	45,700	ND	2.4	ND	76
11/18/93	45.21	9,130	16.8	566.0	2,670	711.0	5,180	54,500	ND	ND	ND	82
11/22/93	49.21	9,810	21.1	289.0	2,760	807.0	5,950	46,600	ND	ND	ND	121
12/03/93	60.46	9,190	20.9	350.0	2,340	735.0	5,560	43,900	ND	ND	ND	85
12/06/93	63.21	7,650	18.0	251.0	2,070	629.0	4,700	42,500	ND	ND	ND	93
TFF-SEPI												
10/05/93	1.25	2,910	39.5	459.0	1,140	164.0	1,140	7,360	ND	ND	ND	.
10/07/93	3.21	7,860	38.7	1120.0	2,900	588.0	3,250	20,300	ND	21.0	ND	120
10/11/93	7.29	6,270	38.5	850.0	2,340	437.0	2,640	16,300	ND	22.0	ND	113
10/14/93	10.21	5,450	34.3	737.0	2,030	398.0	2,280	15,900	ND	22.0	ND	90
10/18/93	14.33	6,780	42.9	999.0	2,540	524.0	2,720	15,800	ND	27.0	ND	113
10/21/93	17.21	4,480	33.7	473.0	1,370	262.0	2,180	13,300	ND	23.0	ND	108
10/25/93	21.21	2,120	26.7	204.0	674	149.0	1,100	7,930	ND	ND	ND	110
10/28/93	24.21	3,480	38.3	358.0	1,230	247.0	1,640	9,080	ND	25.0	ND	116
11/01/93	28.21	2,920	39.8	276.0	1,060	203.0	1,390	7,340	ND	13.0	ND	109
11/04/93	31.21	3,030	41.3	309.0	985	156.0	1,580	7,330	ND	27.0	ND	145
11/09/93	36.21	2,030	37.5	240.0	703	143.0	947	5,420	ND	25.0	ND	108
11/11/93	38.21	5,610	74.9	843.0	2,460	316.0	1,980	7,490	ND	23.0	ND	99
11/15/93	42.21	4,340	39.1	654.0	1,860	137.0	1,680	11,100	ND	24.0	ND	86
11/18/93	45.21	4,280	34.2	456.0	1,600	269.0	1,960	12,500	ND	21.0	ND	91
11/22/93	49.21	2,990	29.9	250.0	998	154.0	1,590	10,000	ND	23.0	ND	86
11/29/93	56.42	4,650	43.1	343.0	1,520	459.0	2,320	10,800	ND	43.0	ND	100
12/03/93	60.46	3,120	35.9	308.0	1,040	254.0	1,510	8,700	ND	23.0	ND	95
12/06/93	63.21	3,470	33.7	357.0	1,170	222.0	1,720	10,300	ND	20.0	ND	91
12/09/93	66.21	3,250	31.3	292.0	1,040	197.0	1,720	10,400	ND	23.0	ND	98
TFF-UVI												
10/05/93	1.25	1,860	38.8	332.0	601	10.0	920	4,790	ND	ND	ND	.
10/07/93	3.21	5,480	37.8	914.0	1,710	ND	2,860	14,500	ND	17.0	ND	118
10/11/93	7.29	4,880	37.5	748.0	1,570	25.0	2,340	13,000	ND	16.0	ND	.
10/14/93	10.21	3,850	31.0	573.0	1,260	40.0	1,980	12,400	ND	18.0	ND	89
10/18/93	14.33	6,020	42.7	935.0	2,150	227.0	2,710	14,100	ND	23.0	ND	122
10/21/93	17.21	4,070	37.3	406.0	1,260	126.0	2,280	10,900	ND	19.0	ND	113

Table A4-7 (continued)

Date sampled	Elapsed time (days)	Total BTEX (µg/L)	BTEX (% of TPH)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	Total xylenes (µg/L)	TPH* (µg/L)	1,2-DCA (µg/L)	TCE (µg/L)	EDB (µg/L)	Surrogate** (% recovery)
<i>TFF-UVI (continued)</i>												
10/25/93	21.21	1,660	20.6	161.0	497	60.0	945	8,070	ND	ND	ND	95
10/28/93	24.21	2,640	42.5	283.0	851	68.0	1,440	6,210	ND	20.0	ND	118
11/01/93	28.21	1,360	16.9	93.0	164	ND	1,100	8,030	ND	6.9	ND	99
11/04/93	31.21	2,700	39.0	269.0	917	152.0	1,360	6,930	ND	22.0	ND	108
11/09/93	36.21	2,050	36.9	245.0	711	155.0	940	5,560	ND	22.0	ND	108
11/11/93	38.21	4,360	61.5	753.0	1,790	41.0	1,780	7,090	ND	20.0	ND	89
11/15/93	42.21	3,600	41.4	265.0	1,150	181.0	2,000	8,690	ND	6.5	ND	77
11/18/93	45.21	3,930	35.7	409.0	1,410	234.0	1,880	11,000	ND	20.0	ND	72
11/22/93	49.21	2,380	31.0	188.0	737	31.0	1,420	7,670	ND	19.0	ND	88
11/29/93	56.42	4,290	41.7	324.0	1,380	387.0	2,200	10,300	ND	35.0	ND	92
12/03/93	60.46	2,190	37.1	215.0	534	4.5	1,430	5,900	ND	12.0	ND	97
12/06/93	63.21	2,490	32.8	286.0	803	88.0	1,310	7,580	ND	17.0	ND	88
12/09/93	66.21	2,490	28.5	206.0	626	34.0	1,630	8,730	ND	20.0	ND	93
<i>TFF-UVO5</i>												
10/05/93	1.25	ND	.0	ND	ND	ND	ND	57	ND	ND	ND	.
10/07/93	3.21	76	.9	11.0	25	2.0	38	8,540	1.6	2.3	ND	56
10/11/93	7.29	30	3.9	3.1	13	ND	14	764	ND	ND	ND	.
10/14/93	10.21	62	2.0	9.1	21	4.9	27	3,040	2.0	2.4	ND	59
10/18/93	14.33	569	32.7	90.0	215	32.0	232	1,740	2.4	12.0	ND	73
10/21/93	17.21	453	32.6	47.0	152	31.0	223	1,390	1.4	10.0	ND	97
10/25/93	21.21	29	9.3	1.7	11	1.7	15	311	.9	1.2	ND	84
10/28/93	24.21	162	32.6	16.0	58	8.0	80	497	3.4	7.9	ND	98
11/01/93	28.21	288	30.3	21.0	101	22.0	144	949	.6	6.8	ND	95
11/04/93	31.21	392	34.1	41.0	142	31.0	178	1,150	.8	15.0	ND	102
11/09/93	36.21	242	37.6	25.0	86	22.0	109	644	.9	16.0	ND	74
11/11/93	38.21	1,130	28.0	190.8	462	70.9	405	4,030	1.8	27.5	ND	104
11/15/93	42.21	3,630	76.7	375.0	1,150	85.0	2,020	4,730	ND	13.0	ND	86
11/18/93	45.21	1,100	32.0	115.0	381	85.0	2,160	3,440	ND	4.1	ND	77
11/22/93	49.21	1,080	20.9	72.0	214	100.0	593	5,160	ND	7.5	ND	90
11/29/93	56.42	2,060	44.8	150.0	649	206.0	1,050	4,600	ND	14.0	ND	102
12/03/93	60.46	935	39.3	81.0	256	68.0	529	2,380	ND	5.2	ND	97
12/06/93	63.21	1,500	35.2	163.0	466	100.0	765	4,260	ND	11.0	ND	103
12/09/93	66.21	1,840	29.8	138.0	523	119.0	1,060	6,170	ND	12.0	ND	104
<i>TFF-EOO6-AQ</i>												
10/26/93	22.38	ND	.	ND	ND	ND	ND	.	ND	ND	ND	93
11/29/93	56.42	ND	.0	ND	ND	ND	ND	35	ND	ND	ND	84

Note: . Indicates analysis not performed.

ND: Not detected at or above limit of detection.

*Total Petroleum Hydrocarbons (Window: C6 to C12).

**Chlorobenzene (QC Limits: 50 to 150).

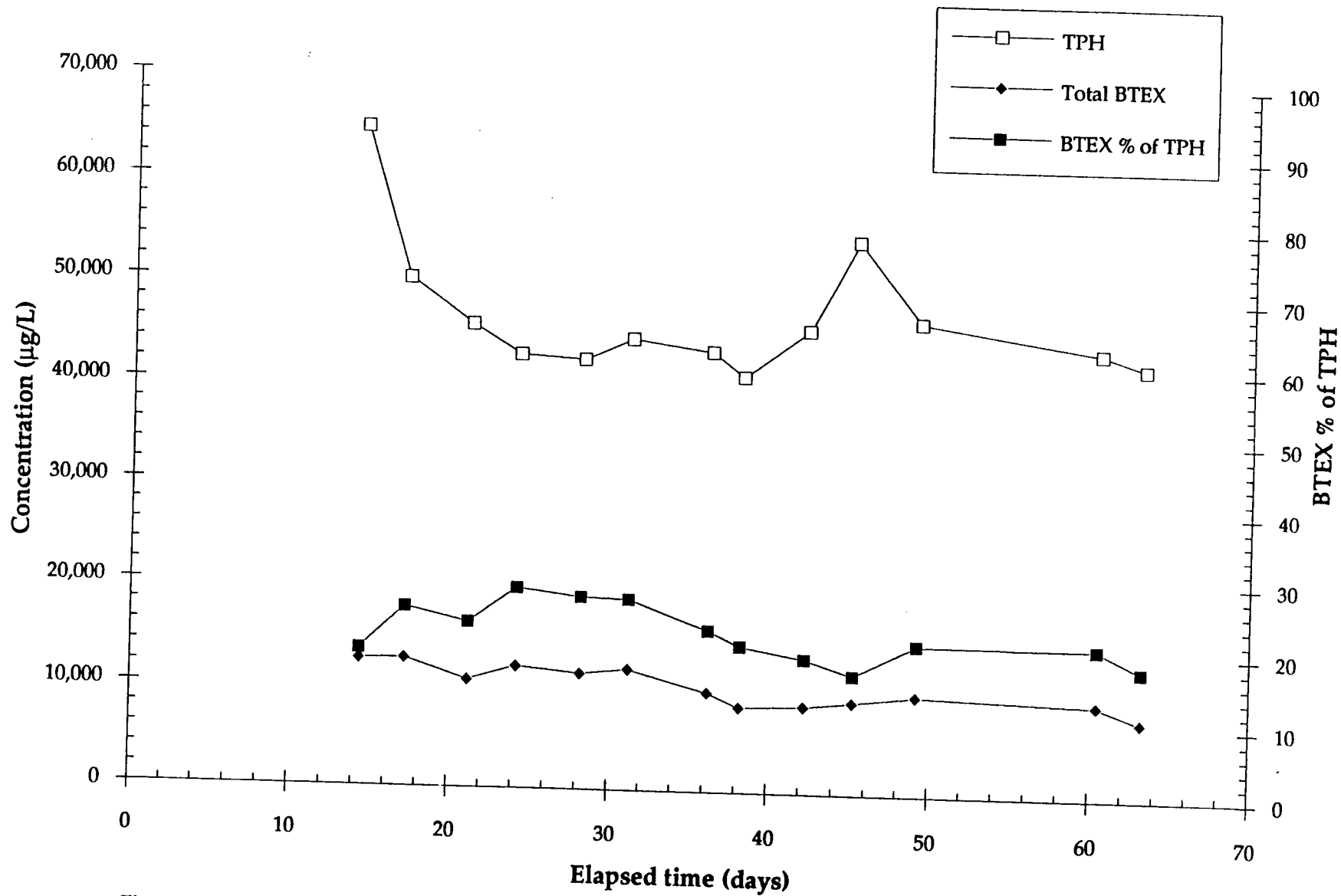


Figure A4-6. Aqueous TPH and total BTEX concentrations measured from the MEGA-AQ sampling port during ARV.

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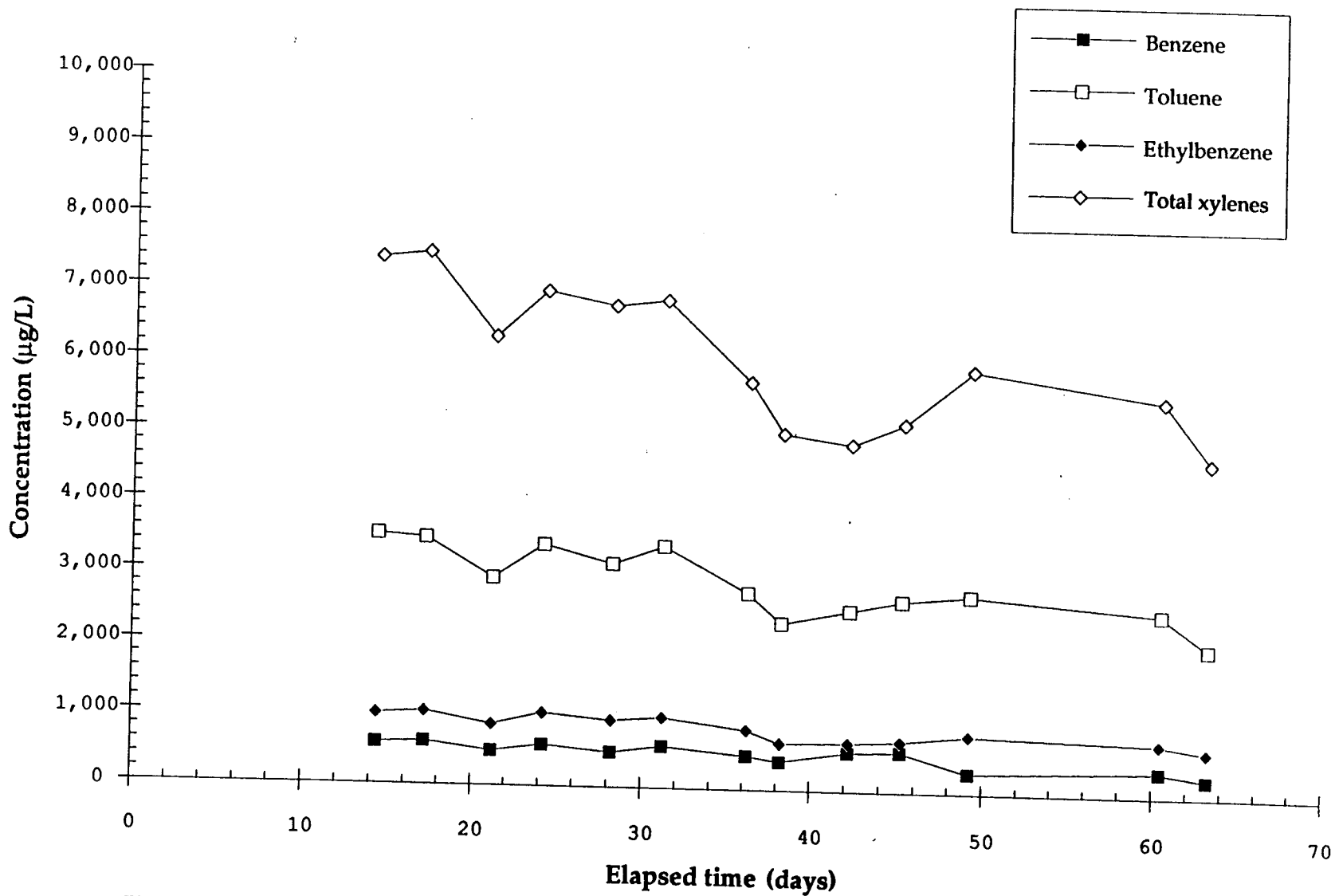


Figure A4-7. BTEX component aqueous concentrations measured from the MEGA-AQ sampling port during ARV.

collected from ICE-IN, I006-VPR, and individual well heads contained high VOC concentrations.

ICE-IN is the designation for the internal combustion engine vapor stream influent sampling port (Fig. 3, main text). Hydrocarbon concentrations in extracted vapor were initially around 6,000 ppmv (Fig. A4-8). After 10 days of continuous extraction, hydrocarbon concentrations decreased to around 3,000 ppmv. TPH concentrations consistently averaged around 82% of total hydrocarbons. Hydrocarbon concentrations varied during the ARV project due to operational changes in the vapor treatment system. By the end of continuous operations, hydrocarbon concentrations in extracted vapor declined to around 1,000 ppmv. Table A4-8 summarizes ARV project vapor analytic results.

Total BTEX concentrations decreased from around 1,000 ppmv to less than 300 ppmv during the ARV project and accounted for less than 14% of the TPH (Fig. A4-9). Concentrations of individual BTEX components were below 500 ppmv and are shown in Fig. A4-10. The largest increase was observed at about 28 days of continuous operation. Relative BTEX-component concentrations in extracted vapor were similar to those in extracted ground water.

ICE-OUT is the designation of the internal combustion engine effluent sampling port that we monitored for air compliance purposes (Fig. 3, main text). Concentrations of total BTEX were typically less than 1.0 ppmv.

CFO is the designation for the air stripper off-gas carbon treatment effluent sampling port. We monitored vapor samples from CFO daily, typically detecting less than 1 ppmv total nonmethane hydrocarbons (Fig. 3, main text).

MEGA-HC is the designation for the skimmed gasoline sampling port on the condensed fluid oil-water separator effluent (Fig. 3, main text). Table A4-9 lists the ten most prevalent components of each gasoline sample collected during the second steam pass of DUSDP and the ARV phase after September 16, 1993. The composition of condensed gasoline did not vary significantly during the ARV project.

References

- U.S. Environmental Protection Agency (EPA) (1985), National Primary Drinking Water Regulations, 40 CFR Part 141, Federal Register 50:46936.
- Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88/039, December 1988, page 46.
- "Principles of Environmental Analysis," Analytic Chemistry, 55, 2210-2218, December 1983, American Chemical Society.
- Standard Methods for the Examination of Water and Waste Water, 18th Edition, 1992.

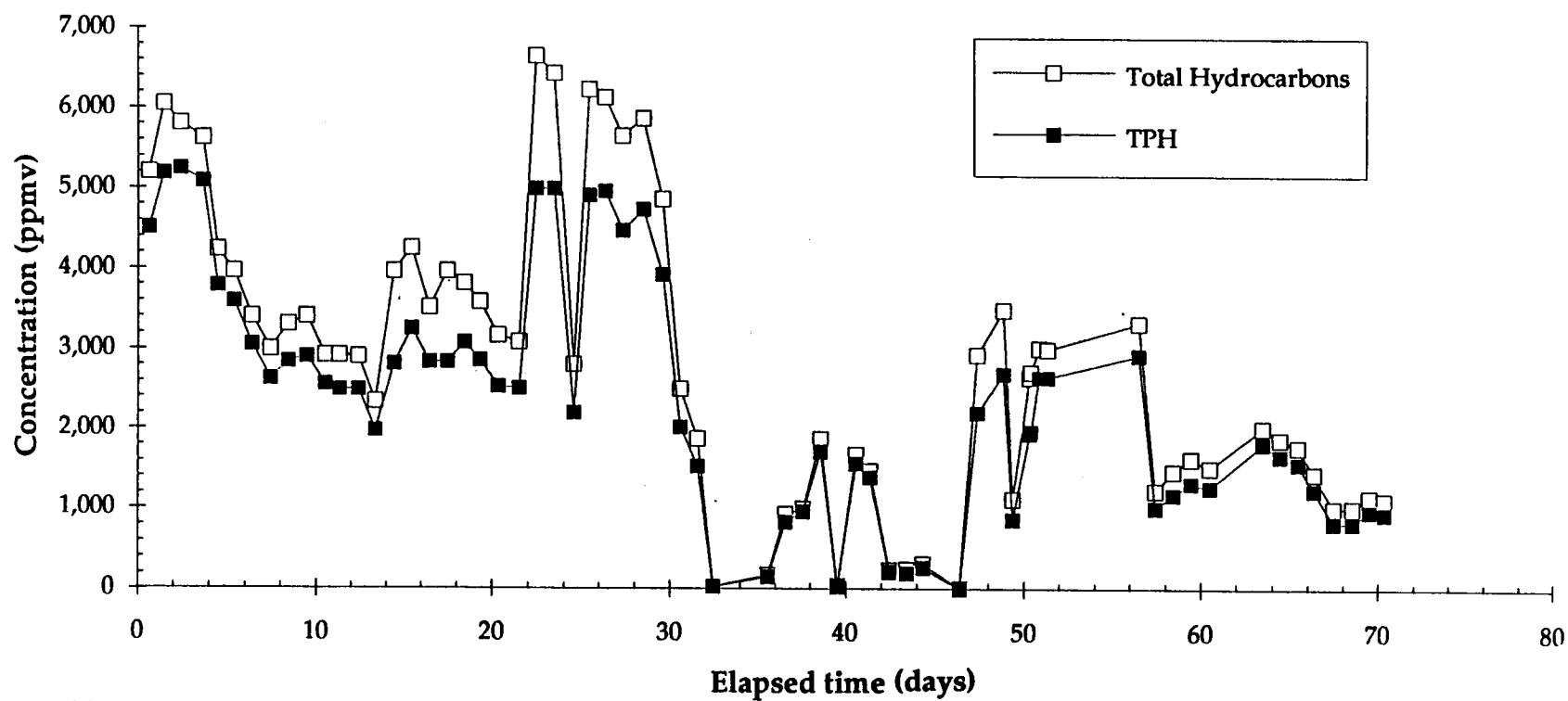


Figure A4-8. Vapor-phase total hydrocarbons and total petroleum hydrocarbons measured from the ICE-IN.

Table A4-8. ARV project vapor analytic results.

Date sampled	Elapsed time (days)	Total BTEX (ppmv)	BTEX (% of TPH)	Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total xylenes (ppmv)	TPH* (mg/L air)	TPH* (ppmv)	HC** (mg/L air)	HC** (ppmv)
<i>TFF-ICE-IN</i>											
10/04/93	0.67	842.0	18.7	77.0	279.0	82.0	404.0	15.9	4,510	18.3	5,200
10/05/93	1.50	915.0	17.6	113.0	326.0	82.0	394.0	18.3	5,190	21.3	6,050
10/06/93	2.46	18.5	5,250	20.5	5,810
10/07/93	3.67	790.0	15.5	96.0	308.0	68.0	318.0	17.9	5,090	19.8	5,630
10/08/93	4.50	624.0	16.5	78.0	225.0	56.0	265.0	13.4	3,790	14.9	4,240
10/09/93	5.42	12.7	3,590	14.0	3,970
10/10/93	6.42	435.0	14.2	49.0	157.0	41.0	188.0	10.8	3,060	12.0	3,400
10/11/93	7.46	427.0	16.2	42.0	146.0	41.0	198.0	9.3	2,630	10.6	3,000
10/12/93	8.46	10.3	2,850	12.0	3,310
10/13/93	9.50	10.2	2,910	12.0	3,400
10/14/93	10.54	427.0	16.7	39.0	142.0	43.0	203.0	9.0	2,560	10.3	2,920
10/15/93	11.38	8.8	2,490	10.3	2,920
10/16/93	12.42	8.8	2,490	10.3	2,910
10/17/93	13.42	7.0	1,980	8.2	2,340
10/18/93	14.50	324.0	11.5	39.0	108.0	30.0	147.0	9.9	2,820	14.0	3,970
10/19/93	15.50	11.5	3,250	15.0	4,260
10/20/93	16.50	10.0	2,840	12.4	3,520
10/21/93	17.50	11.0	2,840	14.0	3,970
10/22/93	18.50	268.0	8.7	28.0	96.0	23.0	119.0	10.8	3,080	13.5	3,820
10/23/93	19.38	10.1	2,860	12.6	3,580
10/24/93	20.38	8.9	2,530	11.0	3,170
10/25/93	21.50	642.0	25.6	41.0	183.0	69.0	349.0	8.8	2,510	10.9	3,090
10/26/93	22.50	18.0	5,000	23.5	6,660
10/27/93	23.50	17.6	5,000	22.7	6,440
10/28/93	24.58	430.0	19.5	32.0	142.0	44.0	212.0	7.7	2,200	9.9	2,810
10/29/93	25.50	17.3	4,920	22.0	6,240
10/30/93	26.38	17.5	4,970	21.6	6,140
10/31/93	27.38	15.8	4,480	19.9	5,660
11/01/93	28.54	1,540.0	32.5	89.0	487.0	167.0	800.0	16.7	4,740	20.7	5,880
11/02/93	29.63	13.8	3,930	17.2	4,870
11/03/93	30.58	7.1	2,020	8.8	2,500
11/04/93	31.58	465.0	30.4	29.0	144.0	50.0	242.0	5.4	1,530	6.6	1,880
11/05/93	32.46	0.1	36	0.1	37
11/08/93	35.58	12.0	7.9	ND	4.4	ND	7.1	0.5	151	0.6	178
11/09/93	36.58	229.0	27.5	11.0	61.0	31.0	126.0	2.9	832	3.3	926
11/10/93	37.58	3.4	960	3.5	993
11/11/93	38.63	356.0	20.8	38.0	158.0	28.0	131.0	6.0	1,710	6.6	1,870
11/12/93	39.54	0.1	36	0.1	39
11/13/93	40.58	5.5	1,560	5.9	1,670
11/14/93	41.38	4.9	1,390	5.2	1,470
11/15/93	42.46	39.0	18.3	11.0	13.0	2.7	11.4	0.7	213	0.8	235
11/16/93	43.42	23.0	11.4	3.5	7.6	1.6	9.9	0.7	202	0.8	240
11/16/93	43.46	72.0	5.4	5.7	25.0	7.1	35.0	4.7	1,340	5.2	1,480
11/16/93	43.50	70.0	4.3	6.4	21.0	6.2	36.0	5.7	1,610	6.3	1,790
11/16/93	43.54	155.0	14.2	23.0	65.0	12.0	55.0	3.8	1,090	4.3	1,210
11/16/93	43.58	92.0	5.9	17.0	46.0	7.0	22.0	5.4	1,550	5.9	1,690
11/16/93	43.63	124.0	6.3	20.0	62.0	7.8	34.4	6.9	1,960	7.5	2,120
11/16/93	43.67	52.0	6.4	13.0	25.0	2.7	11.1	2.9	812	3.1	878
11/16/93	43.75	16.0	5.0	4.0	10.0	ND	1.8	1.1	319	1.3	356
11/16/93	43.83	16.0	2.7	3.4	8.4	1.3	3.2	2.1	586	2.3	646
11/16/93	43.92	13.0	2.8	3.6	6.8	ND	2.1	1.6	465	1.9	526
11/17/93	44.04	1.9	545	2.2	616
11/17/93	44.17	ND	ND	0.0	12
11/17/93	44.33	6.1	2.3	1.4	3.5	ND	1.2	0.9	266	1.1	310
11/19/93	46.38	ND	ND	0.0	12
11/20/93	47.38	7.8	2,200	10.3	2,930
11/21/93	48.88	9.5	2,690	12.3	3,490
11/22/93	49.38	42.0	4.9	ND	14.0	5.1	22.6	3.1	865	3.9	1,120
11/22/93	49.46	0.3	86	0.3	85
11/22/93	49.54	ND	.	ND	ND	ND	ND	ND	ND	0.1	16
11/22/93	49.63	163.0	10.4	6.8	56.0	18.0	82.0	5.5	1,560	6.8	1,930
11/22/93	49.67	960.0	34.7	41.0	354.0	93.0	472.0	9.8	2,770	9.7	2,760
11/22/93	49.83	259.0	37.4	14.0	100.0	23.0	122.0	2.4	693	2.6	729
11/23/93	50.04	68.0	3.3	2.8	24.0	8.0	33.0	7.2	2,050	10.0	2,840
11/23/93	50.21	82.0	3.9	4.6	28.0	10.0	40.0	7.3	2,080	10.0	2,830
11/23/93	50.33	78.0	4.0	4.0	28.0	8.8	36.7	6.8	1,940	9.3	2,640
11/23/93	50.42	6.9	1,970	9.6	2,710
11/23/93	50.42	6.6	1,870	9.1	2,570
11/23/93	50.42	7.0	1,990	9.7	2,740
11/23/93	50.89	485.0	18.4	52.0	218.0	38.0	177.0	9.3	2,640	10.6	3,010

Table A4-8 (continued)

Date sampled	Elapsed time (days)	Total BTEX (ppmv)	BTEX (% of TPH)	Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total xylenes (ppmv)	TPH* (mg/L air)	TPH** (ppmv)	HC*** (mg/L air)	HC*** (ppmv)
<i>TFF-ICE-IN (Cont'd)</i>											
11/24/93	51.38	469.0	17.8	52.0	210.0	36.0	170.0	9.3	2,640	10.4	3,000
11/29/93	56.54	425.0	14.6	33.0	154.0	38.0	200.0	10.3	2,920	11.7	3,320
11/30/93	57.46	3.5	1,000	4.3	1,220
12/01/93	58.46	4.1	1,170	5.1	1,460
12/02/93	59.46	200.0	15.3	17.0	81.0	17.0	84.0	4.6	1,310	5.7	1,620
12/03/93	60.50	4.5	1,260	5.3	1,510
12/06/93	63.46	229.0	12.7	16.0	96.0	20.0	99.0	6.4	1,810	7.1	2,010
12/07/93	64.46	5.8	1,660	6.6	1,870
12/08/93	65.46	5.5	1,560	5.2	1,770
12/09/93	66.38	218.0	17.7	21.0	85.0	20.0	92.0	4.3	1,230	5.1	1,440
12/10/93	67.46	107.0	13.0	6.4	38.0	12.0	51.0	2.9	825	3.5	1,000
12/11/93	68.54	2.9	827	3.6	1,010
12/12/93	69.54	3.4	970	4.0	1,150
12/13/93	70.38	92.0	9.9	8.9	27.0	12.0	44.0	3.3	934	3.9	1,110
<i>TFF-CFO</i>											
10/8/93	4.33	ND	.	ND	ND	ND	ND	ND	ND	0.004	1.0
<i>TFF-ICE-OUT</i>											
10/08/93	4.33	1.0	35.7	1.0	ND	ND	ND	0.0	2.8	0.009	2.7
<i>TFF-GIW-815</i>											
11/16/93	43.40	ND	.	ND	ND	ND	ND	ND	ND	0.040	12
11/16/93	43.48	4.0	1,140	4.4	1,250
11/16/93	43.54	218.0	13.3	20.0	124.0	15.0	59.0	5.8	1,640	6.1	1,730
11/16/93	43.58	1,200.0	20.0	34.0	582.0	110.0	470.0	21.0	6,000	23.0	6,570
11/16/93	43.63	554.0	8.6	28.0	350.0	21.0	153.0	23.0	6,430	25.0	6,980
11/16/93	43.67	179.0	3.2	8.9	96.0	8.9	65.0	20.0	5,650	24.0	6,760
<i>TFF-GIW-820</i>											
11/16/93	43.38	2.4	4.1	ND	1.1	ND	1.3	0.2	59	0.25	70
11/16/93	43.39	1.1	6.5	ND	1.1	ND	ND	0.1	17	0.09	24
<i>TFF-GIW-820-Lower</i>											
11/22/93	49.36	11.0	.	ND	7.1	ND	4.2
11/22/93	49.41	ND	.	ND	ND	ND	ND
11/22/93	49.42	396.0	.	18.0	185.0	37.0	157.0
11/22/93	49.44	154.0	14.1	7.7	68.0	15.0	64.0	3.8	1,090	4.3	1,220
11/22/93	49.46	7.4	2,090	8.1	2,300
11/22/93	49.51	13.0	.	ND	7.9	ND	5.0
11/22/93	49.54	5.0	.	ND	ND	ND	5.0
<i>TFF-GIW-820-Upper</i>											
11/22/93	49.36	8.5	7.9	ND	ND	4.8	3.7	0.40	108	0.49	140
11/22/93	49.40	0.70	194	0.87	248
11/22/93	49.42	1.90	547	2.50	720
11/22/93	49.44	5.40	1,520	7.00	1,990
11/22/93	49.46	138.0	7.1	3.4	48.0	17.0	70.0	6.90	1,950	8.90	2,530
11/22/93	49.49	0.10	23	0.10	28
11/22/93	49.50	0.10	30	0.11	31
11/22/93	49.52	ND	ND	ND	ND
11/22/93	49.54	ND	0.0	ND	ND	ND	ND	0.10	29	0.12	34
11/22/93	49.57	0.30	97	0.35	98
11/22/93	49.60	ND	0.0	ND	ND	ND	ND	0.10	31	0.11	31
11/22/93	49.65	0.10	31	0.11	32

. Indicates analysis not performed.

ND: Not detected at or above limit of detection.

*Total petroleum hydrocarbons (Window: C6 to C12).

**Total hydrocarbons (Window: C1 to C12).

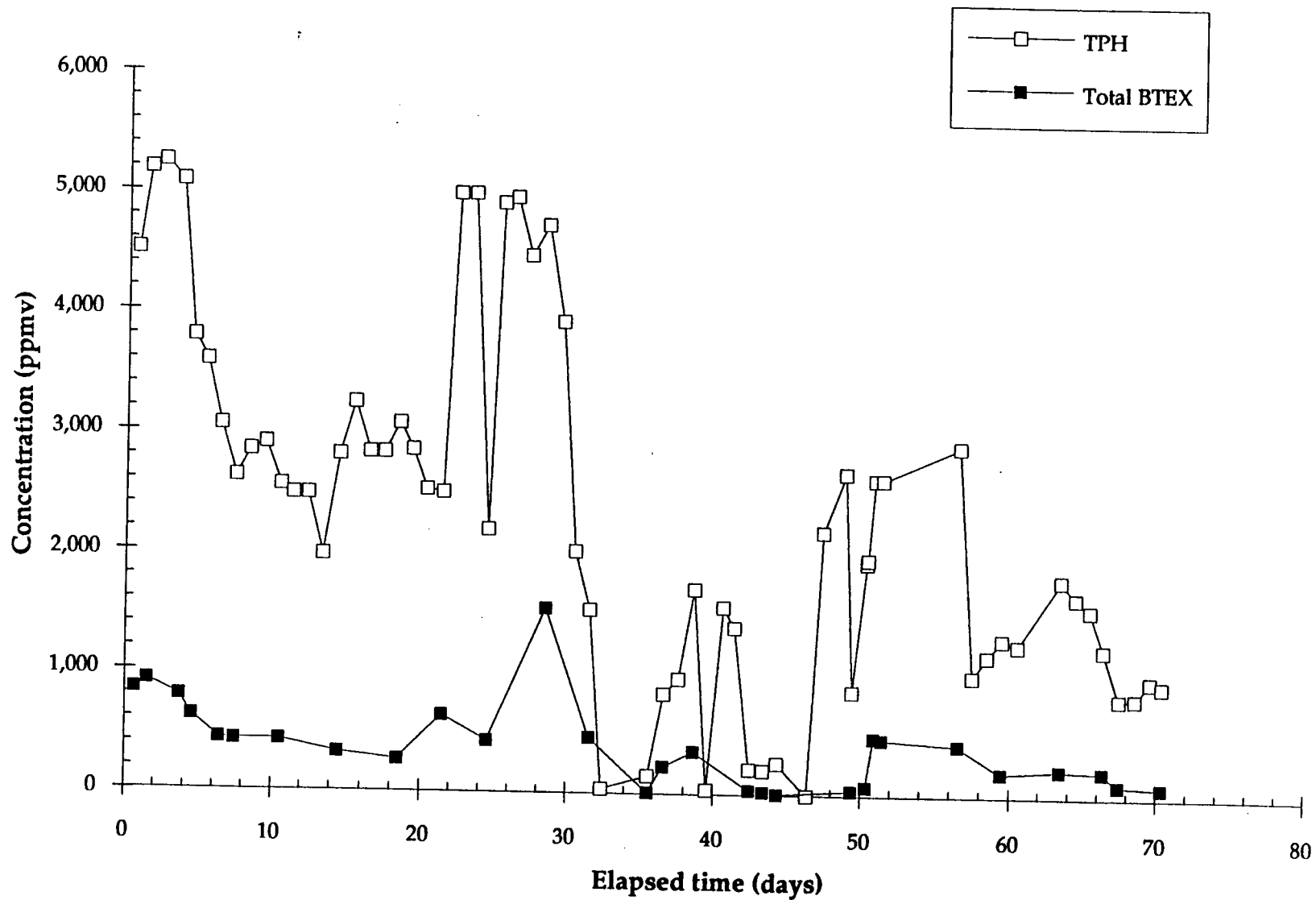


Figure A4-9. Vapor-phase total petroleum hydrocarbon (TPH) and total BTEX concentrations measured from ICE-IN.

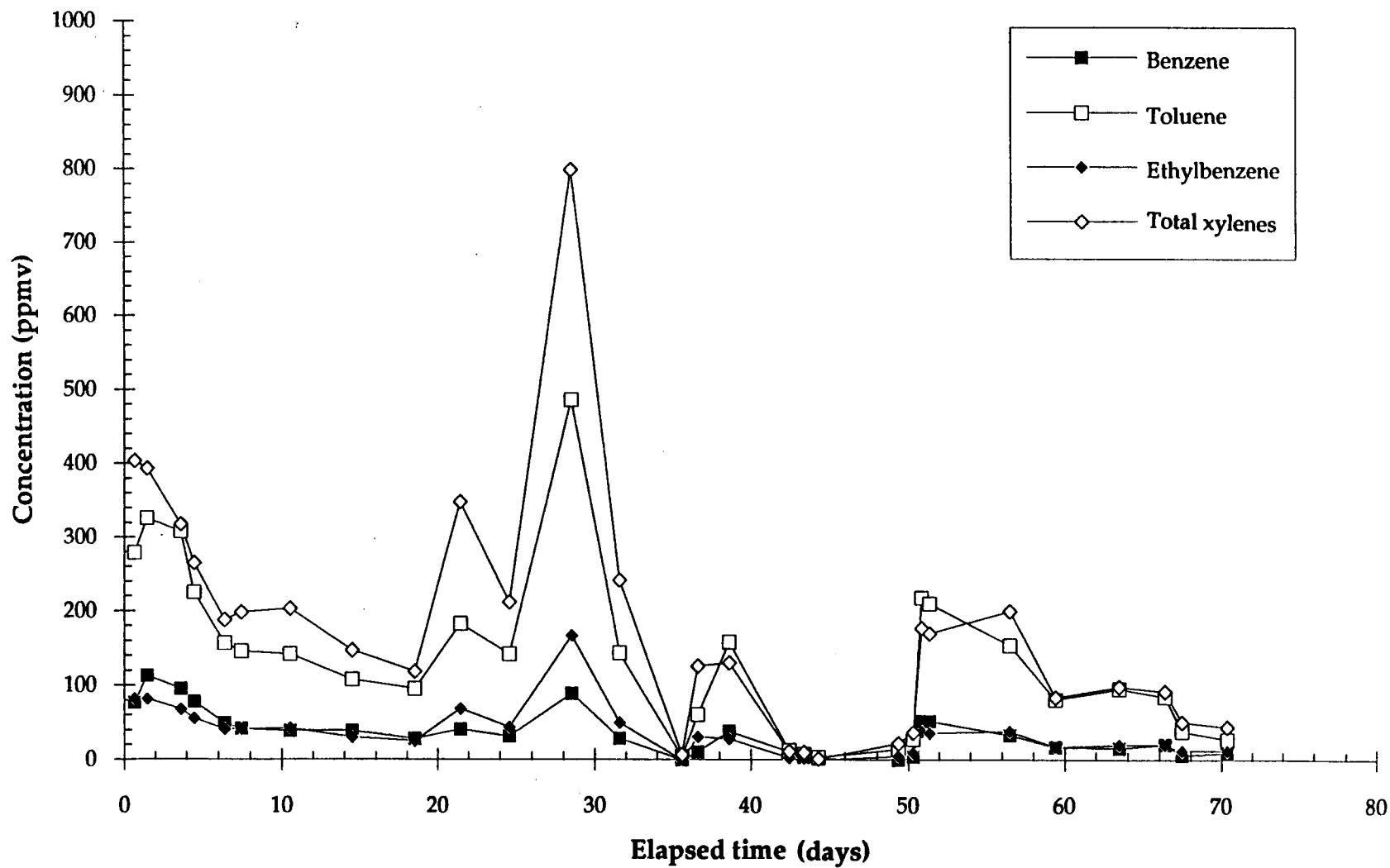


Figure A4-10. BTEX concentrations measured from TFF-ICE-IN.

Table A4-9 - Ten largest identified peaks by GC/MS of MEGA-HC condensed vapor.

Retention time (min)	Tentatively identified compounds	Dates sampled								
		5/25/93	5/27/93	6/3/93	6/15/93	6/17/93	6/21/93	9/16/93	10/13/93	10/25/93
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
1.97	2-methyl pentane	3.4								
2.38	Methyl cyclopentane	3.1								
2.77	2-methyl hexane	6.1	3.6							
2.88	3-methyl hexane	4.1	2.4							
3.19	Heptane	3.6								
4.22	Toluene	12	11	3.9	3.2	2.8				
4.77	Octane		2.4							
5.87	Ethyl benzene		3.2	3.5	3.5	3.1				
6.08	m,p-xylene	15	12	11	9.0	11	4.0	6.8	4.6	4.0
6.49	o-xylene	4.2	4.9	4.9	5.0	4.6	2.7	2.8		
7.55	Propylbenzene				2.8					
7.70	1-ethyl-2-methyl benzene	4.8	6.6	4.5			5.2	7.4	6.4	5.8
7.82	1,3,5-trimethyl benzene		2.6	7.0	8.8	9.7		3.0		
8.28	1,2,4-trimethyl benzene		7.2	2.7	7.0	11	9.6	11.3	10.3	9.6
8.75	1,2,3-trimethyl benzene	3.8		9.1	4.3	4.6	2.0	3.7	3.7	3.4
8.78	1-ethyl-3-methyl benzene			4.5				9.6		
9.22	1-methyl-3-propyl benzene			3.7	3.6	3.7		4.1	4.3	3.9
9.80	1-methyl-2-(1-methylethyl)benzene					3.0	3.0	2.6	3.0	3.0
10.77	1, 2, 3, 5-tetramethylbenzene						2.3			
10.83	1-methyl-2-(2-propenyl)benzene							2.9	3.8	3.9
11.28	C4 alkylbenzene				2.6		1.9			
11.40	Naphthalene					2.8	3.0	2.9	3.8	4.1
13.00	2-methylnaphthalene						2.7		3.4	4.1
13.24	1-methylnaphthalene						2.7		3.4	4.1

Appendix 5

Modeling of ARV Sparging and Electrical Heating Using NUFT and an Ohmic Heating Module, and Related Laboratory Measurements

(C. R. Carrigan and J. J. Nitao, Earth Science Division, LLNL)

Introduction

The Dynamic Underground Stripping Demonstration Project (DUSDP) incorporated several remediation technologies simultaneously to mobilize and extract contaminants from both high- and low-permeability formations in the near-surface hydrologic regime. Understanding how steam injection into soils and ohmic heating (produced by passing electrical currents through the soils) interact to affect the rate of contaminant extraction has been one goal of the project. This understanding is a prerequisite to generalizing the technique for other cleanup sites. This understanding is also necessary if the efficiency of the technique's application at a specific site is to be maximized. To develop a predictive/diagnostic capability, we produced a generalized numerical three dimensional (3D) model of the *in situ* ohmic or joule heating process, which has been coupled to an existing 3D simulator for nonisothermal porous flow and transport (NUFT). This combined joule heating/hydrologic model permits a full simulation of the stripping process in a hydrologic medium of arbitrary complexity.

The ohmic heating program is modular and may either be executed with NUFT or in the stand-alone mode. In stand-alone operation, the program can be used to develop a basic understanding of how electrode placement can affect the current flow and, hence, the volumetric heating rate in a volume having a prescribed electrical conductivity distribution. In the absence of detailed hydrologic, geologic, and electrochemical information, this approach may be preferred during the initial planning phases of a heating and extraction facility. The module can be used to:

- Obtain preliminary estimates of the voltage and current demands on the power supply.
- Test various assumptions on the apometric localization of ohmic heating around electrodes.
- Obtain the effect on joule heating caused by changing electrode placement in either the horizontal or vertical coordinates.
- Determine the best electrode configuration for maximizing the heating rate in specific parts of the hydrologic system.

The module also simulates the application of either single phase or multiphase electrical power to the electrodes, a factor that must be considered in designing and costing an electrical system for a site.

As a module functioning interactively with the NUFT hydrologic program, a variety of complex, mutually dependent processes can be investigated. For example, the injection of steam at a well can affect the electrical conductivity through changes in both the saturation and temperature of the soil. Another phenomenon of interest is the formation of a high resistivity zone around electrodes owing to the drying out of that soil near the electrodes. The formation of such a zone or skin of high electrical resistivity around the electrodes will tend to redistribute ohmic dissipation so that more heating occurs locally near the electrodes rather than uniformly throughout the soil volume under consideration. Another concern that must be addressed during the operations stage is the schedule for injecting steam and for ohmic heating. Because large amounts of energy are expended to heat the soil during the stripping operation, it is desirable to determine the most cost-effective schedule for the steam stripping/ohmic heating process for a particular site.

Air Sparging at TFF

The first problem modeled in support of the ARV phase of operations at Treatment Facility F (TFF) involved the isothermal modeling of air injection and vapor extraction in wells at the gas pad site. For this, NUFT alone was used to develop an isothermal model. The problem involved injecting air in the lower steam zone (LSZ) at an injection well while attempting to remove the air at an extraction well some distance away and downdip (8°). In addition to the downdip tilt between the injection and extraction wells, there was an additional 4° tilt at right angles to the first tilt, placing the injection well downdip from a monitoring well (see Fig. A5-1).

The LSZ was simulated by a tilted rectangular layer (140 m (l) x 126 m (w) x 4 m (d)) that was typically gridded by more than 2,300 3D elements (33 x 22 x 4). The material properties of the layer were chosen to correspond to those of the LSZ. High permeability is a major feature of this zone. Hydrostatic pressure distributions were applied at the sides of the layer to simulate a farfield pressure distribution in the tilted LSZ below the water table. The injection and extraction wells were modeled by assigning a mass injection rate for the injection well and a subatmospheric pressure to the extraction well.

Figure A5-1 shows plan views of the air plume at different times following initiation of the injection process. As its growth proceeded, the plume migrated up and across the tilted layer along the gradient of elevation. Irrespective of the extraction pumping rates downdip at the extraction well, no air from the plume was ever drawn down to the extraction well. This numerical prediction was borne out by the actual tests in which injected air in the LSZ did not reach the extraction well. Some air from the injection well, i.e., the fringe of the plume, did reach the monitoring well about an hour after injection commenced. This behavior was also supported by the observations at the gas pad monitoring well.

These simulations of air sparging indicate that geologic control, i.e., the tilting of the formation, dominated in determining the path of the injected plume. Even very high (214 gal/m) simulated pumping rates from the extraction well did not significantly influence the plume's direction. Considering that the tilt of the LSZ can only be considered at worst to be moderate,

we conclude that very careful placement of injection and extraction wells is necessary if the air sparging process is to be successful for many hydrologic environments. Otherwise, air injection without effective extraction may spread contamination well beyond its original borders.

Ohmic Heating Simulations

With the ohmic heating module coupled to the NUFT hydrologic model, a variety of heating models was investigated. The main thrust of the modeling effort was to investigate the effect of different electrode configurations in a multilayered hydrologic model that also included the temperature, saturation, and medium dependent variations in the electrical conductivity, which are typically associated with the layering of different soil types. The dependence of the electrical conductivity on the temperature, saturation, and soil type was evaluated using the model of Waxman and Smits (1968).

A major change in the ARV heating system was the introduction of long electrodes (approx. 60 ft) that extended across the upper steam zone (USZ), clay confining layer, and LSZ. The original electrodes used in the DUSDP were emplaced only in the clay confining layer. Power levels maintained during the ARV phase were either comparable or less than those used during the DUSDP. In the ARV phase, ohmic heating of the layering resulted in much lower heating rates compared to the DUSDP experience, which could not be explained by differences in power input alone. In addition, large amounts of vapor were removed from an extraction well located centrally between the long electrodes (refer to Section IV in the main report).

A series of different ohmic heating models were examined. The models were based upon the five-layer hydrologic model illustrated in Figure A5-2. This five-layer model includes the three layers of greatest interest to dynamic stripping: an unsaturated, permeable sandy-clay soil (labeled USZ in Fig. A5-4); a saturated, low-permeability clay layer (CON) directly beneath; and another permeable, but saturated, sandy-clay layer (LSZ) beneath the clay layer. In addition, this three-layer arrangement is bounded at the top and bottom by highly conductive and impermeable clay layers whose existence is indicated by well logs.

One effect of short versus long electrodes in this five-layer model is illustrated in the vertical profile of volumetric heating across the five layers in Figure A5-3. Assuming the same power dissipation in both cases, short electrodes in the central clay layer produce a much higher level of volumetric heating (dotted line) than do the longer electrodes (solid line). With the longer electrodes, more power is lost in heating other layers, especially the top clay layer, which is penetrated by the long electrodes. For constant power levels, long electrodes are less capable of focusing ohmic heating into specific layers such as the central clay layer.

The lack of specificity in heating associated with the long electrodes is exacerbated when steam is produced at the electrodes and this steam is free to flow into the layered formation. The value of the ohmic heating technique lies mainly in its ability to heat low-permeability layers that cannot be effectively flushed or heated by steam injection. Thus, when steam is produced at an electrode, two undesirable things occur. First, electrical energy is lost to steam that cannot effectively heat the low permeability layers. Second, the steam flows to other more permeable layers, heating them and also enhancing their electrical conductivity, so that more current flows through them. When vapor extraction from the unsaturated zone is also taking place, the steam

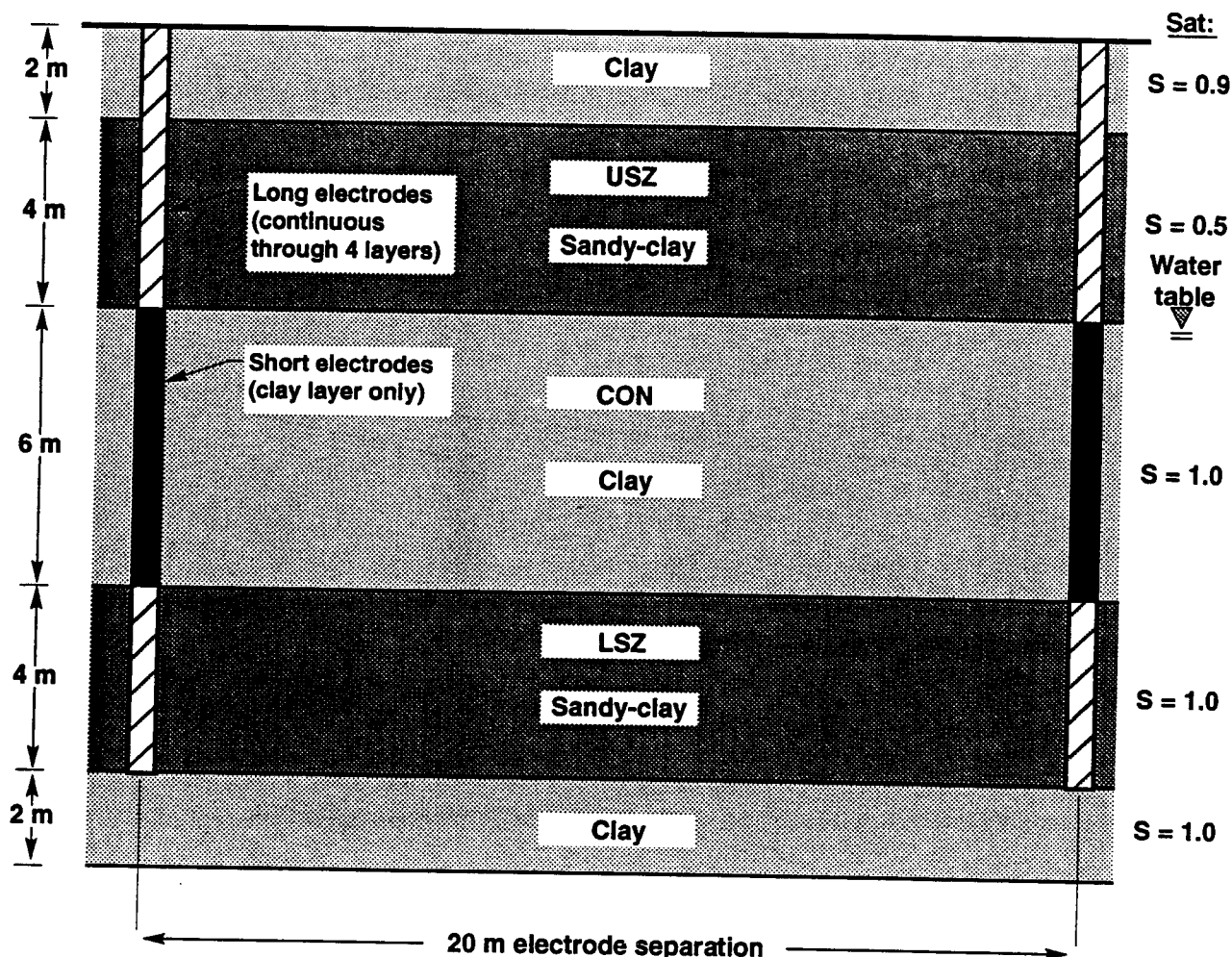


Figure A5-2. Simplified diagram of subsurface geology of heater wells at the TFF site which shows the size of the installed heater electrodes and their as-installed relation to the formation. The short electrodes (solid black) were installed and used during the DUSDP and the ARV phases of activities. The long electrodes (diagonal strips) were installed after the DUSDP in drill-back characterization wells and used exclusively during the ARV phase.

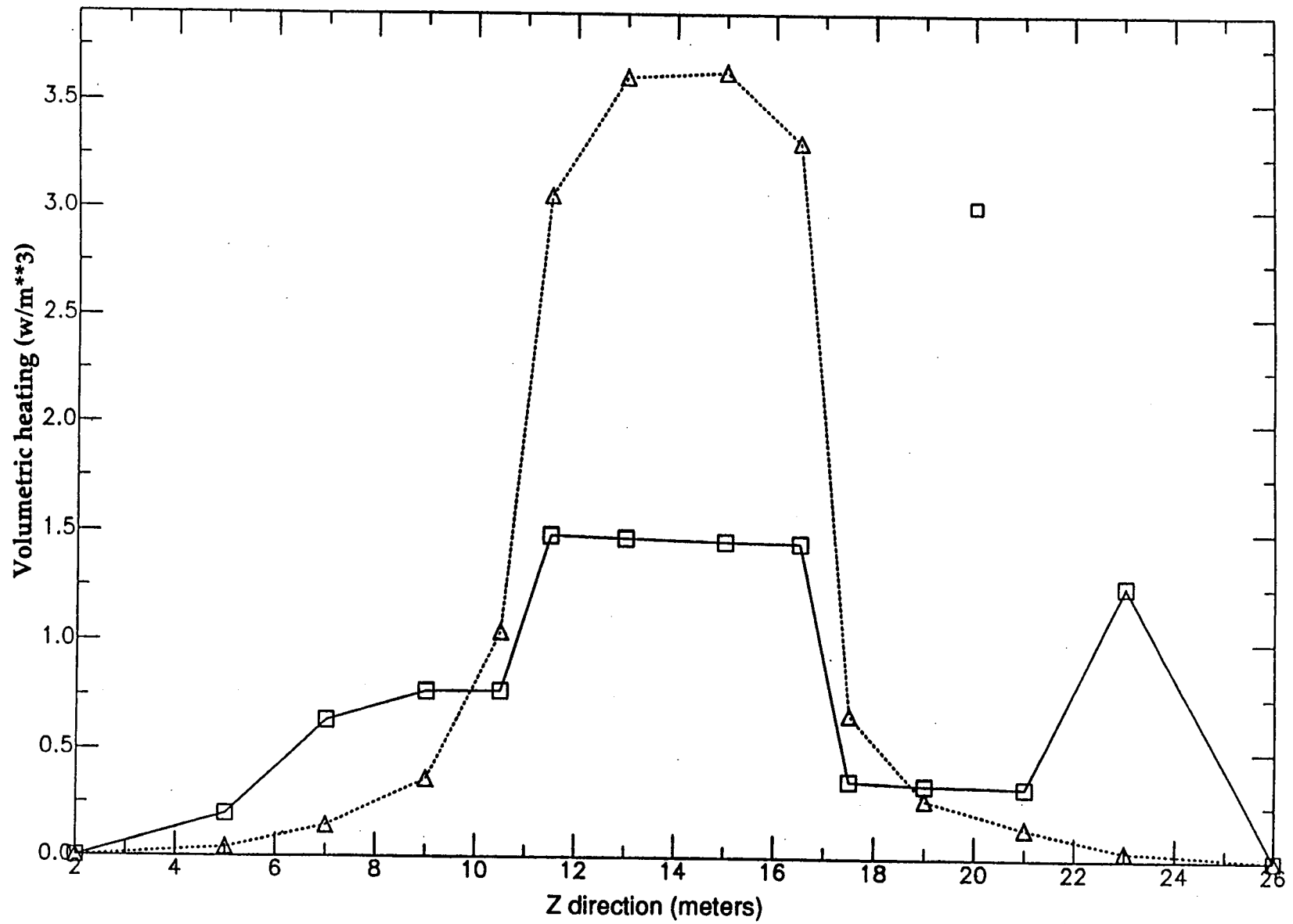


Figure A5-3. Focusing effect of short electrodes is shown in plot of volumetric heating rate versus vertical coordinate (z).

and, hence, the thermal energy is removed from the hydrologic system before it can influence the temperature of the central clay layer by conduction.

The five-layer model was used to examine the effect of steam production at the long electrodes. Unlike the short electrodes used in the clay layer, the long electrodes are porous along their length and readily permit the escape of steam that is produced in the electrode wells. To model the effect of steam production on ohmic heating, a small head of steam (approximately 3 psi) was maintained in the two electrode wells. The actual steam head is probably much higher, so that this model is conservative in terms of the effect of steam. Figure A5-4 shows the temperature and volumetric heating distribution in a vertical plane intersecting the two electrodes initially and at a time 5 days into a heating simulation. The temperature plots show a significant increase in the temperature of the partially saturated USZ as steam has gradually flowed into this zone (note the color change between the initial and final times in the upper part of the temperature distributions). The electrical conductivity has also been modified by the flow of steam into the USZ layer. This enhances the volumetric heating in that layer relative to the heating in the underlying clay layer, which is the target of the ohmic heating experiment. This can be seen by comparing the intensity of the color of the horizontal layer CON at the center of the plot to the intensity of the layer USZ immediately above the center. The darker layer at the earlier time becomes the brighter layer after 5 days of ohmic heating.

Conclusion

We have used numerical models to provide a diagnostic understanding of air sparging and the ohmic heating process. In the case of air sparging, we find that small inclinations of the injected layer tend to dominate the flow of the air plume. Even if large amounts of water are extracted, it is unlikely that the air plume can be made to flow downdip toward an extraction well. The modeling suggests that air sparging facilities must be carefully designed to take into account, through the placement of extraction and injection wells, the dominating effects of weak layer inclinations on determining the path of the injected air plume.

The various ohmic heating models that have been studied indicate that long, porous electrodes appear to produce effects that are counter to the goal of ohmic heating, which is to heat selected layers that are not amenable to infiltration by injected steam. For a given power input, long electrodes tend to divert current away from the target layers. When steam is produced at the electrodes, this diversion can be increased. For optimal heating of the target layer, it can be argued that any steam production should take place within the target layer and not at the electrodes themselves.

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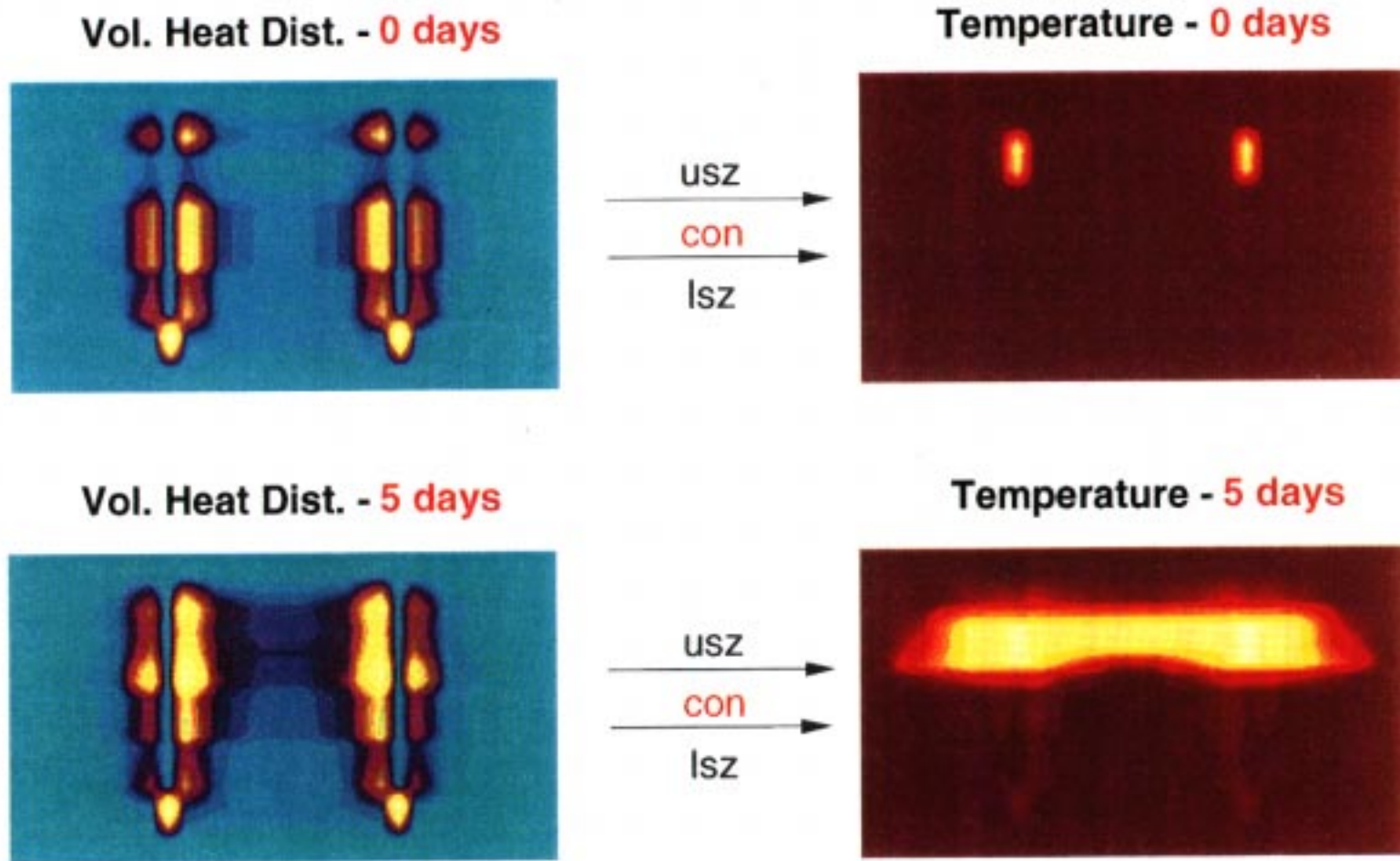


Figure A5-4. The effect of steam production in long electrodes is simulated using the 5-layer model.

Laboratory Determinations of Xylene Solubility as a Function of Temperature and Pressure

(Kevin Knauss, Earth Sciences Division, LLNL)

We made "reversed" (i.e., equilibrium approached from both super- and undersaturation) measurements of the liquid/liquid solubility of p-xylene in water as a function of temperature and pressure. Temperature was varied from 25° to 150°C and pressure was varied from 15 to 7,500 psi. Experiments were run in high-pressure vessels modified to contain a flexible pure gold bag (220cm³) fitted with a removable pure titanium closure. The high-pressure vessel was heated in a large tube furnace mounted on a rocking device, and was inverted to allow sampling of the aqueous phase. This device is ideally suited for mutual solubility measurements.

Sampling of the aqueous fluid was achieved by withdrawing through a titanium tube that exits through the head of the stainless steel high-pressure vessel and a special high-pressure valve (needle and valve block made of titanium) directly into a glass gas-tight syringe. The syringe is preloaded with methanol to maintain xylene in solution at room temperature and pressure. Pressure is maintained constant, even during sampling, by pumping water into the high-pressure vessel using a computer-driven precision HPLC pump, which collapses the gold bag.

The sample/methanol mixture was immediately (<2 min) analyzed for xylene via GC using purge and trap extraction and detection via an FID (flame ionization). The GC analyses (including purge and trap processing) and data reduction are all accomplished using an HP chemstation. Calibration was via xylene standards prepared in methanol.

These data were used to calculate thermodynamic quantities pertinent to p-xylene solution in water (Knauss and Copenhaver, 1994).

For this project, however, the desired quantities were the solubility of liquid xylene and the Henry's law coefficient (H) as functions of temperature (T).

The solubility of liquid xylene is determined directly by the measurements. These data are plotted in Figure A5-5. For the purposes of this project, the data are fit to a simple third order polynomial, and the regression results are displayed on the plot.

Knowing xylene solubility as a function of T, we can calculate H via the expression:

$$H = pp/x$$

where: pp = partial pressure of xylene at the temperature and pressure of interest

x = solubility of xylene (as mol fraction) at the temperature and pressure of interest.

The pp of xylene at any temperature and pressure is derived from knowing the system total pressure and Pvp (the vapor pressure) of pure xylene. This is conveniently calculated using Antoine's equation:

$$\ln P_{vp} = a - (b/T+c)$$

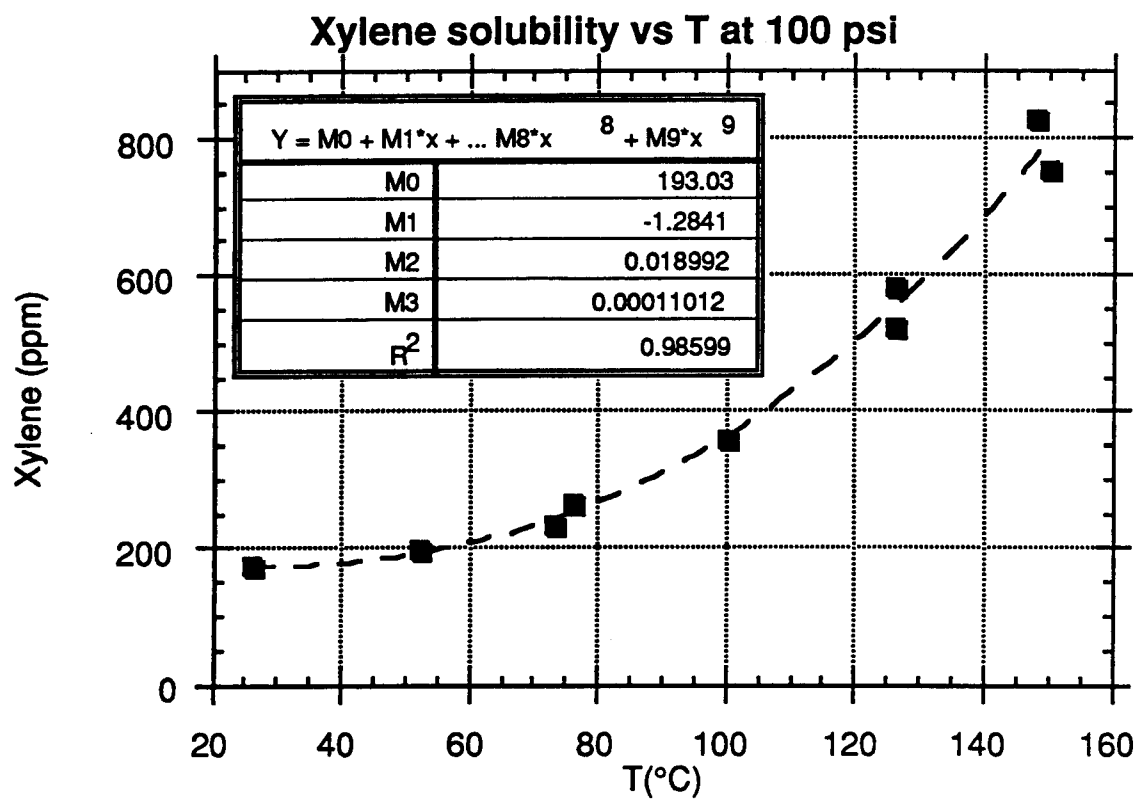


Figure A5-5. Experimentally determined (squares) xylene solubility as a function of temperature.

and the appropriate constants (a,b,c) extracted from any number of compilations (e.g. Reid *et al.*, 1987).

Perhaps more directly useful than the Henry's law coefficient is the Dimensionless Distribution Coefficient (DDC). It can be shown (Knauss and Copenhaver, 1994) that with reasonable assumptions: $DDC = H/RT$, where R = the gas constant and the other variables are previously defined. Figure A5-6 contains plotted values of $\log DDC$ vs T . The data are fit to a simple third order polynomial, and the regression results are displayed on the plot.

The reader wishing a more detailed accounting of the experimental procedures, the relationship of solubility to pressure, and the calculated thermodynamic quantities derived from the data is referred to Knauss and Copenhaver (1994).

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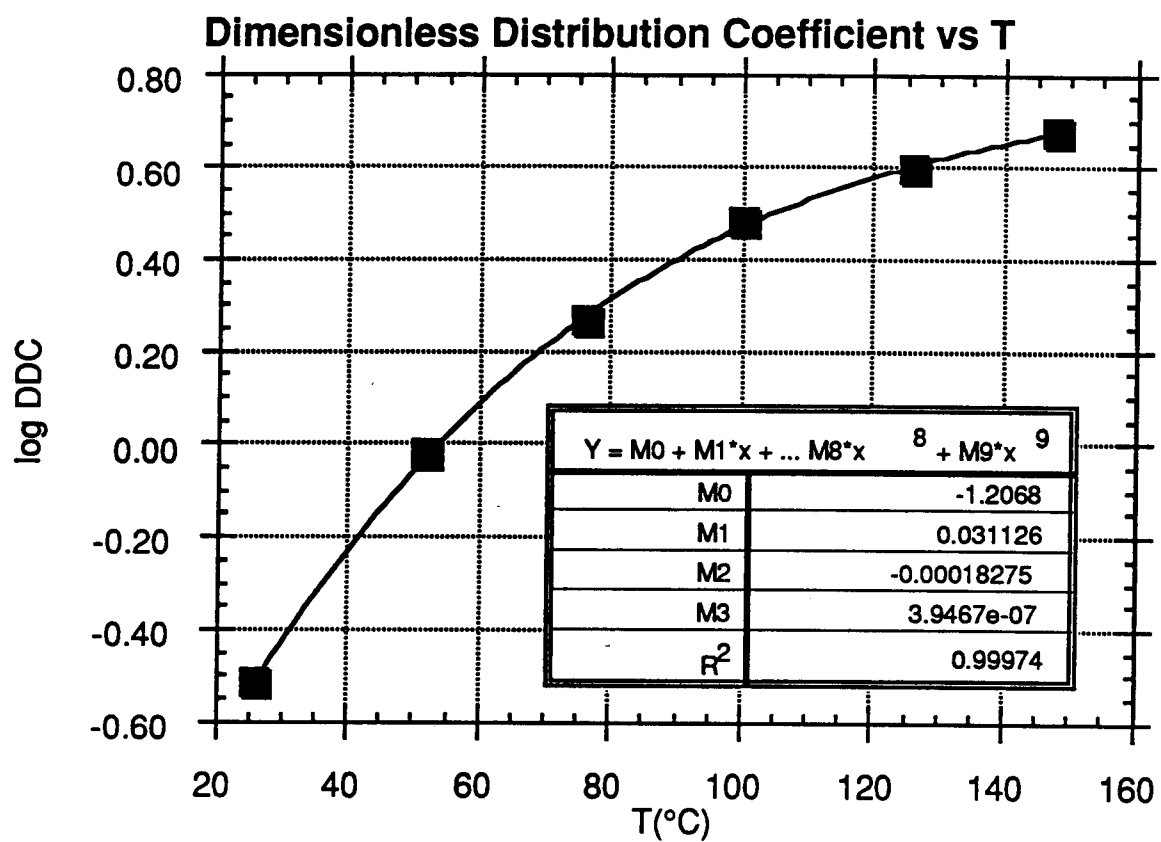


Figure A5-6. Dimensionless distribution coefficient as a function of temperature.

Appendix 6

Structure and Flow of Data through the LLNL ERD Environmental Data Management System

(C. Suzanne Chamberlain and Patricia L. Ottesen, Environmental Restoration Division, LLNL)

Introduction

This section describes the structure and flow of data in the data management system used by the Environmental Restoration Division (ERD) of the Environmental Protection Department (EPD) of Lawrence Livermore National Laboratory (LLNL) to store and archive data from the Accelerated Removal and Validation (ARV) Project.

The structure is based on two relational databases that are closely correlated. The first database handles sample tracking. The second database handles data such as sample location, media, analytical results, and some geological information (Fig. A6-1). These two databases are maintained on a VAX 6310 with VMS using INGRES relational database software. The flow of data, both hard copy and electronic, follows a model that tracks information from sampling plan through storage to archiving. The steps in the process include chain-of-custody (CoC) tracking of the sample, analytical result receipt, the application of quality control procedures, and the electronic use of data in decision support tools, such as risk assessment and compliance monitoring.

Structure and Flow

A sample plan was developed to establish the frequency, method, and location of samples to be taken (Fig. A6-2). Field log books and CoC forms confirm the collection of samples according to the plan. A document control number is assigned to the samples based on the field log book used. A carefully controlled system of field log book labeling permits electronic tracking of an environmental sample from field collection through analytical result receipt as well as tracing back to the log book for any given analyte, should details of sampling conditions be needed. Samples are sent on to analytical laboratories where they are given unique log numbers.

The important fields in each SPACT record are document control number, analytical laboratory, analytical lab log number, sampling location identification, sampling date, and analysis requested. Dates tracked include those for receipt of the CoC form and analytical results, and date of entry. SPACT also includes invoice information. Receipt of official printed analytical results and invoices cause database records to be updated based on the document control number and location. A data record is marked complete only when all analytical results have been received. Thus, completion of a record confirms that all requested analyses have been performed and reported.

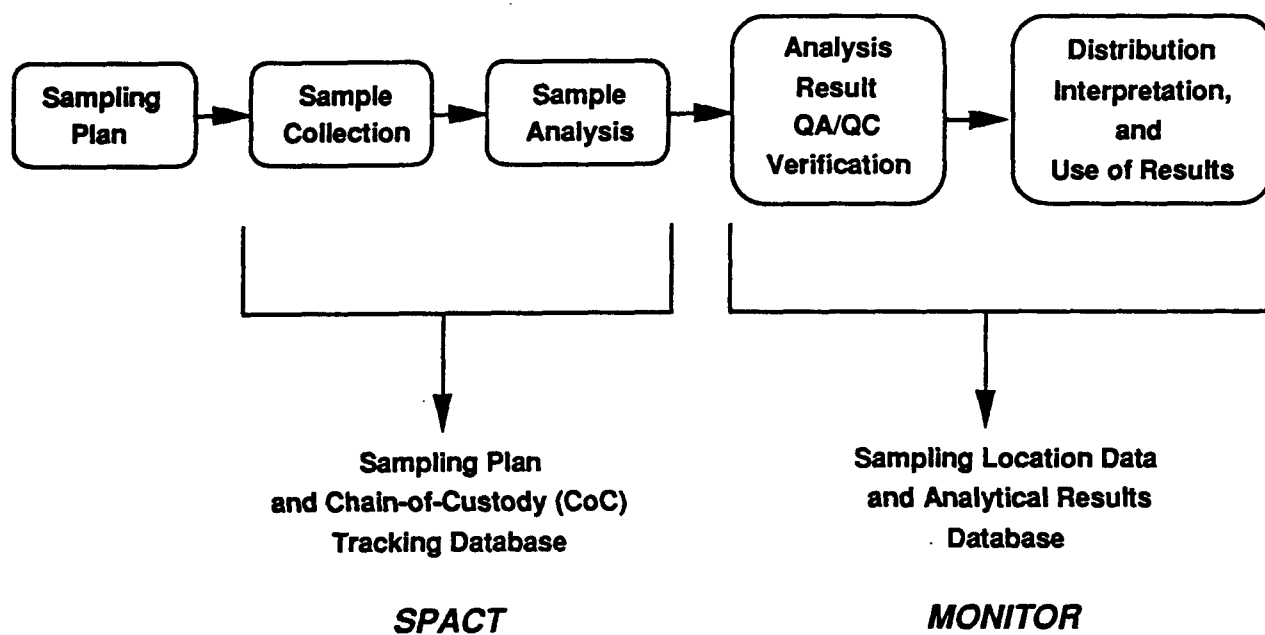


Figure A6-1. Environmental data flow.

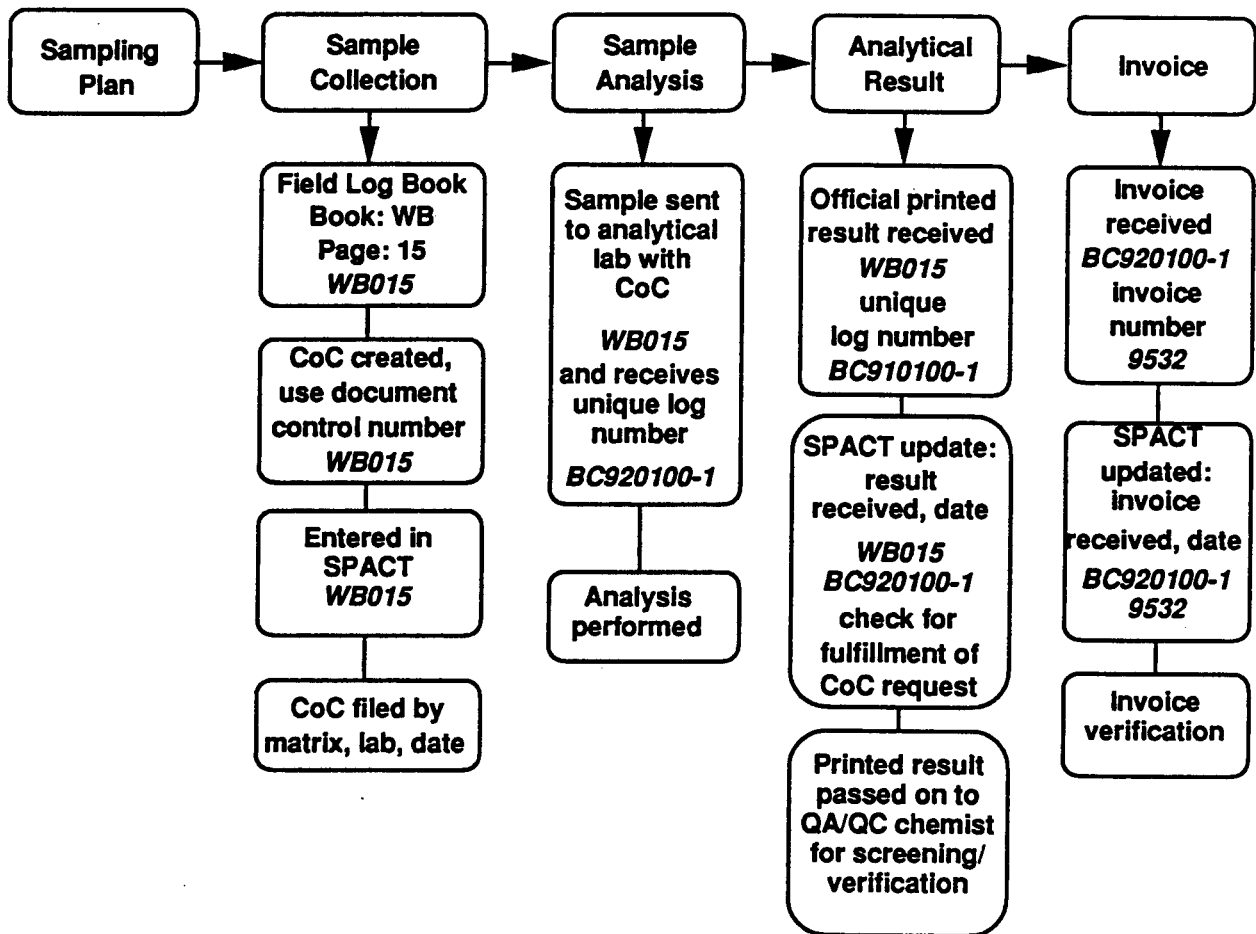


Figure A6-2. Environmental data flow - SPACT Database.

Analytical results are stored in a separate, but correlated, relational database based on sampling location, log number, and date. This database is called MONITOR (Fig. A6-3) and is related to SPACT by identical fields: document control number, sampling location, sampling date, analytical laboratory, and requested analysis. Additional information collected for each sample and analyte includes requester, project, sample media, sample type, units, error, detection limit, dilution factor, and dates of extraction, analysis, and entry, together with comments and special notes. Sources of data in this database include geologic borehole logs, surveyor reports, field measurements, laboratory measurements, calculated or reduced data, and test conclusions. Types of data to be stored have included descriptive sample location information, such as coordinates, elevations, lithology, and screened intervals of monitoring installations, as well as measurements and analytical information, including physical and chemical parameters, media identification, and ground water elevation measurements.

Data verification and validation are achieved through a combination of methods. Hand-entered data are run through a series of computerized verifications that check for duplication, empty fields, and reported results not consistent with reported detection limits. Data are also thoroughly checked by a second person before being formally added to the database. Electronically delivered laboratory data are groomed to fill in empty fields and insure consistency in fields such as sample location, project, media, and type. Computerized verifications are also run on electronic data, and a second person checks sample descriptor fields before formal addition to the database. Random audits are done to verify electronically delivered results against official printed results. Analytical results added to the database are validated through review by qualified chemists. Final verification is done by project scientists who request and use the data. They report outliers, anomalies, and any other inconsistencies indicated by comparison with similar data and historical trends to both the data management team and the quality control chemists who review and qualify or correct the data as appropriate.

The MONITOR database also contains fields dedicated to quality control. Such fields include flags, indicating analytical result qualification and data quality level. The result qualifier flags are absent from a routine report, but may be included to show nondetection, dilution greater than one, rejection, or any of several other types. Data quality levels can range from EPA-approved methods performed by a certified laboratory to quick, approximate field analyses.

Printed copies of the data received are filed by location and chronological order in a data reference library. The originals are retained for data submittal to regulators when required.

The operations data are stored in spreadsheets on Macintosh computers at the Gas Pad. Complete backups on this data occur on a weekly basis with incremental backups occurring daily. These weekly backups are currently stored in T4383. Plans are being developed for fire-resistant storage. To allow for long-term access to the backed-up data, each month a tape is marked to save until data generation ceases. At the time data generation ceases, three complete archival backups will be performed and stored in separate locations. This procedure will provide the highest level of availability of the data in the future.

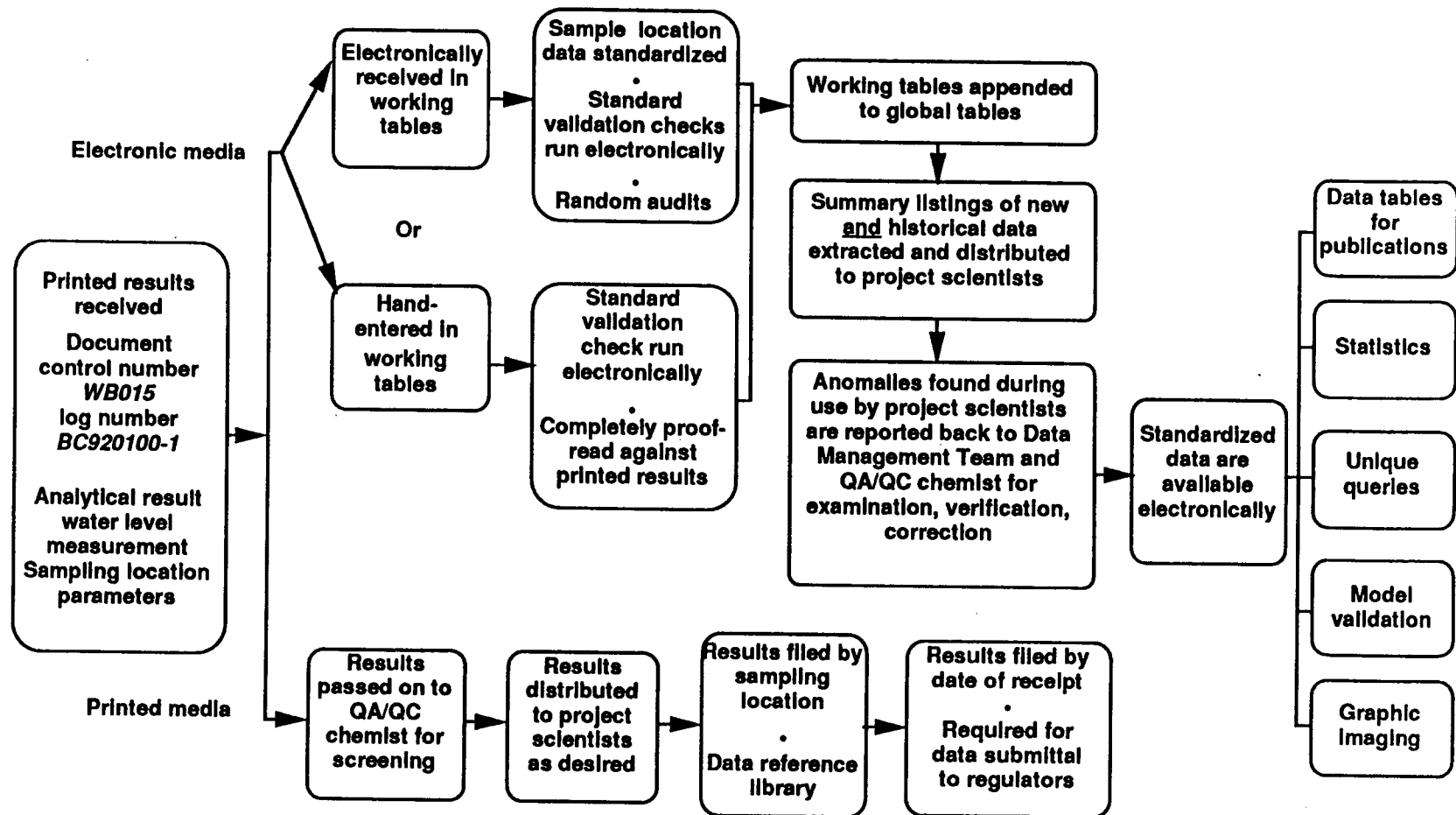


Figure A6-3. Environmental data flow - MONITOR database.

Conclusions

There are many advantages of this integrated centralized data management system. The use of such a system promotes and provides a consistent data set of known quality, which is available to all. Single entry for multiple use allows quality assurance and quality control to be performed equally for all data. Once an error is discovered and corrected, the data will be correct for all future uses. Interesting correlations and trends in the data may become obvious from linked extractions in the future.

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